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Prepared for

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Franklin A. Ayer, Compiler

Research Triangle Institute
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EPA Project Officer: Robert V. Hendriks

Industrial Environmental Research Laboratory
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Prepared for

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PREFACE

These proceedings for the "Symposium on Iron and Steel Pollution Abatement Technology for 1980" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (IERL–EPA), Research Triangle Park, NC. The symposium was conducted at the Benjamin Franklin Hotel in Philadelphia, PA, November 18-20, 1980.

This symposium was convened to provide participants an opportunity to exchange information on technology problems related to air, water, and solid waste pollution control in the iron and steel industry. The program included a Keynote Address, presentations on the environmental aspects of a proposed formcoke demonstration plant, and the future of steel technology and the environment. Sessions were conducted on air pollution abatement, covering coke plant emission control, fugitive emission control, innovative air pollution technology, iron and steelmaking emission control, and inhalable particulates; water pollution abatement, covering recycle/reuse of water, coke plant wastewater treatment and coke plant wastewater new developments; and a session on solid waste pollution abatement.

Mr. Robert V. Hendriks, Chemical Engineer, Chemical Processes Branch, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, was Project Officer and General Chairman for the symposium.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, NC, was symposium coordinator and compiler of the proceedings.

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*Denotes speaker

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OPENING SESSION

Chairman: Robert V. Hendriks
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

STATEMENT OF SYMPOSIUM OBJECTIVES

Robert V. Hendriks
Industrial Environmental Research Laboratory
Research Triangle Park, NC

Being here in Philadelphia, I am reminded of one of this country's most remarkable citizens - Benjamin Franklin. If Franklin were alive, he would share many interests with those of us here today. In a sense, he was a composite of all of us in this room. He had a keen interest in science and technology and made many important scientific contributions in his day. He was an inventor, with several notable inventions to his credit. He was an author with papers on many subjects. He was a dedicated public servant. Yet the most remarkable thing about Franklin was his vision and courage and his desire to make life better for his fellow man.

Franklin can well serve as a symbol for this Symposium as we, too, try to make life better through an improved environment. During the next few days we will focus our attention on technological solutions to environmental problems in the iron and steel industry. Air, water, and solid waste pollution control technology will be covered. You will hear about innovative technologies and ideas, improvements in design and operating procedures, and the results from the latest assessment programs. We have a number of excellent papers and excellent speakers representing a wide cross section of industry, government, and contractor viewpoints. This year, the symposium even takes on an international flavor with speakers from Canada and the Peoples Republic of China. But the papers not only convey information, but serve as a means of generating questions and discussion from you, the audience.

In additon to this opening session, the Symposium is divided into three sessions - Air, Water, and Solid Waste. Each speaker will have 20 minutes for his presentation. To encourage questions, we have grouped papers by similar topics to get several views of the same topic. After presentation of all the papers in the group, the speakers will sit on a panel to answer any questions that you might have concerning their papers or particular area of expertise.

I see a number of familiar faces here today. Based on last year's attendance, almost one-fourth of us work for federal and state regulatory and enforcement agencies, one-fourth of us work for steel-producing companies, and the remaining one-half of us represent contractors and other interests. Although we frequently sit on opposite sides of the table, we all have at least one similar goal - to improve environmental control in the steel

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industry. I think our diversity is a good thing. This is an open forum in which we encourage a variety of viewpoints. We invite you to ask the tough questons and bring important issues to the forefront.

I welcome you here on behalf of my colleagues in the Industrial Environmental Research Laboratory and hope you enjoy the symposium.

SMARTER REGULATION: GETTING BUSINESS TO FIND A BETTER WAY

BY WILLIAM DRAYTON

Rules, even the very best possible rules, are crude and wasteful. They can't do what the manager on the spot can: find the most efficient way of getting whatever the public wants done done. Worse, an unrelieved regime of rules takes away a manager's incentive to find solutions, let alone to innovate.

No one can measure just how wasteful our rule-dominated approach to regulation is. We don't have a practical alternative in place with which to compare it. However, it's clear that the cost is enormous.

In 1977 EPA stopped to ask if all the regulations it was writing one by one* made sense when applied to specific plants. At the first plant it found that the cost of removing one pound of dust from the emissions of different regulated processes ranged from less than 25¢ to over one hundred dollars. Subsequent studies--both of particular plants and of the comparative cost effectiveness of the Agency's many regulations--confirm that wide variations between the costs per pound removed are common.

Obviously, we'd all be better off if we could control more 25¢, or even $1 pounds and forget about an equal number of the very expensive hundred dollar pounds. A DuPont study of fifty of its plants suggests that the company could cut its $106 million annual hydrocarbon pollution control bill over 60 percent if it were allowed to make one simple change to the mix of its controls.

However, under the traditional "command and control" regulatory regime neither the company or those charged with regulating it could make this sort of common sense trade. Every process must remove a specific percent of the pollution it would otherwise emit by a specific, legally binding deadline. A rule is a rule.

---

*Like many other regulatory agencies EPA writes regulations fitted to the particular characteristics of specific production processes, e.g., paint spray booths, degreasing operations, printing presses, oil storage tanks.

EPA is changing that. Its air pollution rules are no longer chiseled in concrete. If a company can make a more sensible counterproposal, one that will save the company money and still get the environmental job done, EPA will happily accept.

Instead of "command" (rule writing) and "control" (enforcement), EPA is moving to a quite fundamentally different "command, counterproposal, and control" approach.

Here's how EPA's new counterproposal approach works.

EPA begins this new approach much as it did before: it writes the best, most responsible rules it knows how. However, it then encourages business to trade reduction requirements, substituting more efficient, sometimes innovative controls for relatively expensive requirements, both within and across plant lines. To provide the necessary incentive EPA's policy leaves the savings to business. And the Agency is working to create new market structures to facilitate this trading.

Offset Trading

It is illegal to build a new facility in an area where the air is too filthy to meet basic health standards, if doing so will aggravate the area's air quality problem. To prevent an intolerable conflict between the need for local economic growth and modernization on the one hand and this statutory public health requirement on the other, EPA first adopted the idea that one source of pollution could meet its environmental obligation by getting another source to take additional control actions.

The offset policy requires the new facility to control its emissions as tightly as possible and then to offset what it can't control with reductions of the same pollutants elsewhere in the community. Thus, for example:

- When the State of Pennsylvania successfully attracted Volkswagen to a Western Pennsylvania site, one element in its package of inducements was the provision of sufficient offsetting reductions of the pollutants that cause photochemical oxidants in the area to meet this requirement. It provided these offsets itself in large part by shifting to water-based rather than petroleum-based asphalt in its road building and repair work in 16 nearby counties. The VW plant now needs additional offsets and it and the state are exploring several prospects at nearby steel facilities.

- Similarly, the Chambers of Commerce in Shreveport, Louisiana, and Oklahoma City, Oklahoma, made room for new GM plants in their communities by inducing local oil companies to close marginal facilities and to reduce storage tank emissions.
- General Portland Cement paid Parker Brothers $520,000 to install dust collectors on its facility in New Braunfels, Texas, so that General Portland could add a new coal-fired preheater to its plant there without pushing the area over the health standard for particulates.

Even during our first two years' experience with this new tool, it has made a significant difference. Despite the barrier of novelty and the difficulty of knowing what possible, economically attractive control alternatives exist outside any one manager's sphere of control, business has completed 650 such offset trades during these start-up years. The banking reform outlined below will make trading much easier and no doubt increase its volume substantially.

The Bubble

The "bubble" allows managers to escape the narrow vision of existing process-by-process regulation and to look at their facilities as a whole. As they plan their counterproposal they can imagine that their facilities are covered by an enormous plastic bubble. As long as the bubble doesn't let more pollution escape than the sum of all the process regulations it covers would, the manager can go about controlling the several sources of pollution under the bubble as he thinks makes most sense. As long as air quality is protected, the bubble can stretch well beyond one plant's boundaries. It covers all existing processes.

Although the bubble policy was only announced nine months ago, industry has already proposed over seventy, quite varied bubble trades. For example:

- 3M's Bristol, Pennsylvania, plant has proposed to bubble ten tape coating lines. It would save several million dollars by using water-based coatings and a new solventless "hot melt" process to reduce emissions more than EPA's standard requires on some lines and cut back controls on others.
- Weyerhauser proposes to save $5 million in capital costs, $200,000 in annual operating costs, and up to 1 million barrels of oil a year at its Plymouth, North Carolina, plant by increasing its use of wood in an existing oil/wood waste boiler and shutting down several oil-only boilers. These trades would hold particulate emissions constant.

- Andre Greenhouses proposes to switch from low sulfur oil to a mix of high sulfur oil and natural gas at three locations in Pennsylvania.

As we gain more experience with this central innovation, as we work out its bugs and loosen some of its restrictions as we gain confidence, we can expect it to become more and more important.

Banking

In order to further facilitate controlled trading in emission reductions EPA is also assisting states in developing "Banking" regulations. "Banking" will provide additional cost savings and incentives for innovation by allowing businesses to achieve extra control (more emission reduction than otherwise required) at the most cost-effective time and then using those reductions as credits toward emission reduction requirements at some later time.

* * * * * * * *

This new approach promises to be the most significant change in how this country regulates since the 1930's.

- It returns to business the flexibility to figure out the best way of getting the job done. (It leaves the regulatory agency with the responsibility of checking to ensure performance.)

- It provides for the first time the same powerful, bottom line incentive for business to find new, more efficient methods of control that managers now have to cut production costs. "Command and control" provides no such incentive to innovate. A plant engineer that found a better way of controlling pollution in one area until now could not benefit elsewhere. The much increased rate of control technology innovation this reform promises is its most important benefit. Without this incentive, the environmental movement is in very deep danger. The volume of pollution compounds every year as population and the economy compound. But there is never any more air, land, or water. Consequently, the cost of any given level of environmental safety increases each year. The only way to avoid this dangerous result is the increased rate of control technology innovation this new approach would incite.

- It should go a long way to improving industry's dismal failure to operate and maintain control equipment properly. Now the average "complying" source of air pollution emits more than 25 percent more pollution than it legally should, even netting out periods when it emits less. This problem, already critical, will get steadily worse as equipment ages unless we give plant managers and engineers new incentives. Now they commonly neither understand nor care much about this equipment. However, once they design their own controls, they will have both the necessary understanding and a paternal professional psychic investment in making them work.

- It should soften the adversarial, overly lawyer-dominated relationship now common between managers and regulators by getting both sides to talk more about _how_ to get a job done rather than only about _whether_ _or_ _when_ it should be done.
- It will save business a great deal of money. (With air and water pollution cleanup costs alone running at roughly $40 billion per year, even a small 10 percent savings would be worth $4 billion a year. The greater efficiencies I think likely and/or applying the reform to broader areas of regulation could of course multiply the savings.)

The same counterproposal principle EPA is currently demonstrating in the air pollution area could be applied widely across government's other regulatory programs.

Addendum

Freeing the Bubble from Unnecessary Constraints

Our first eight month's experience with the Bubble has convinced us we need to relax several unnecessary constraining rules.

The Bubble policy asked persons who wanted to use the Bubble approach at their plants to estimate through "models" the impact of their emissions on air quality by methods more stringent than were used to set existing emission limits, a common practice when reviewing "variances." In some cases, the models showed micro-violations at one or more points, technical violations which prevented the bubble even when the bubble would reduce overall pollution.

We are modifying our estimating procedures. The policy now says that between similar pollution sources we will ask only if total emissions from the bubble counterproposal are the same or less than from the existing regulation. If so, no models are needed. We will only model in cases where the proposed changes will increase emissions on balance.

The bubble policy said that to make the counterproposal federally enforceable, each had to be treated as a revision to the applicable State regulation. Revisions are procedurally slow and require multi-layer government reviews.

Many businesses have claimed the prospect of such delay prevented them from designing a counterproposal.

The State of New Jersey proposed in its regulations a generic provision allowing bubbles under specified conditions. On October 6, EPA accepted this New Jersey approach. EPA specifically announced that it would henceforth allow states to adopt generic review procedures for bubble applications, thereby making unnecessary a formal revision to state regulations for each bubble.

ENVIRONMENTAL ASPECTS OF THE PROPOSED INLAND STEEL FORMCOKE DEMONSTRATION PLANT

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Michael O. Holowaty, Senior Advisor, Research
Harold L. Taylor, Senior Advisor, Research

Inland Steel Company
East Chicago, Indiana

ABSTRACT

A brief history of the development of formcoking processes for metallurgical coke production is presented and blast furnace evaluations of formcoke produced with the FMC formcoking process are reviewed. The flow sheet for the Inland Steel Formcoke Demonstration plant is presented and the emissions control equipment and environmental advantages of the FMC formcoke process are discussed based on the results of recently completed engineering studies.

REVIEW OF FORMCOKE PROCESSES

The concept of a formcoke process was proposed by Dawson in 1856. At the present time, almost every steel producing country has a project or an idea for formcoking. The reason for the drive to drastically change or to completely replace the conventional by-product coking process lies in the fact that the formcoke process is better suited for present conditions. The by-product coking process was satisfactory when the supply of coking coal was abundant, air pollution standards more lenient,and labor cheap. This is no longer the case. Environmental control is of paramount importance; the cost of labor and equipment have skyrocketed, and the supply of inexpensive coking grade coals is being exhausted.

The first recorded commercial production of partially devolatilized coal agglomerates in the United States took place in November, 1933, near the Champion coal preparation plant of the Pittsburgh Coal Company located approximately 32 km west of Pittsburgh. Eventually, two more production units were added in 1934 and 1936, and the average production for the three kiln unit was about 5900 Mg per week of low temperature coke known as Disco fuel.

The Disco plant operations were discontinued in 1946. There was little activity in the formcoking field until about 1951, when the Belgian Iniex process and the British National Coal Board process reached the experimental stage.

General speaking, the formcoking processes developed since 1951 fall into one of the following three categories:

1. Hot briquetting - coal acting as the binder
2. Hot balling - coal or coal tar pitch acting as the binder
3. Cold briquetting of char - coal tar pitch acting as the binder

Hot Briquettes - Ancit Process(1)

The hot briquetting process was originally developed in Europe. The Iniex process, the B.B.F.-Lurgi process, the Australian Auscoke, and the Luxembourg Ancit processes are typical for this approach to the coal agglomerate problem. The Ancit process is shown diagramatically in Figure 1.

The production of formcoke by this process requires approximately 65% inert low volatile coal (anthracite) or char to be preheated to about 590°C. At this point, it is thoroughly mixed with a strongly coking coal so that the temperature of the blend increases to almost the temperature of incipient fluidity (400-430°C). At this point, the blend is force fed between two briquetting rolls and the resulting briquette is green formcoke. It can be completely coked and devolatilized by heating to about 870°C for 1 hour. Subsequently, it is cooled to 120°C and used in the blast furnace.

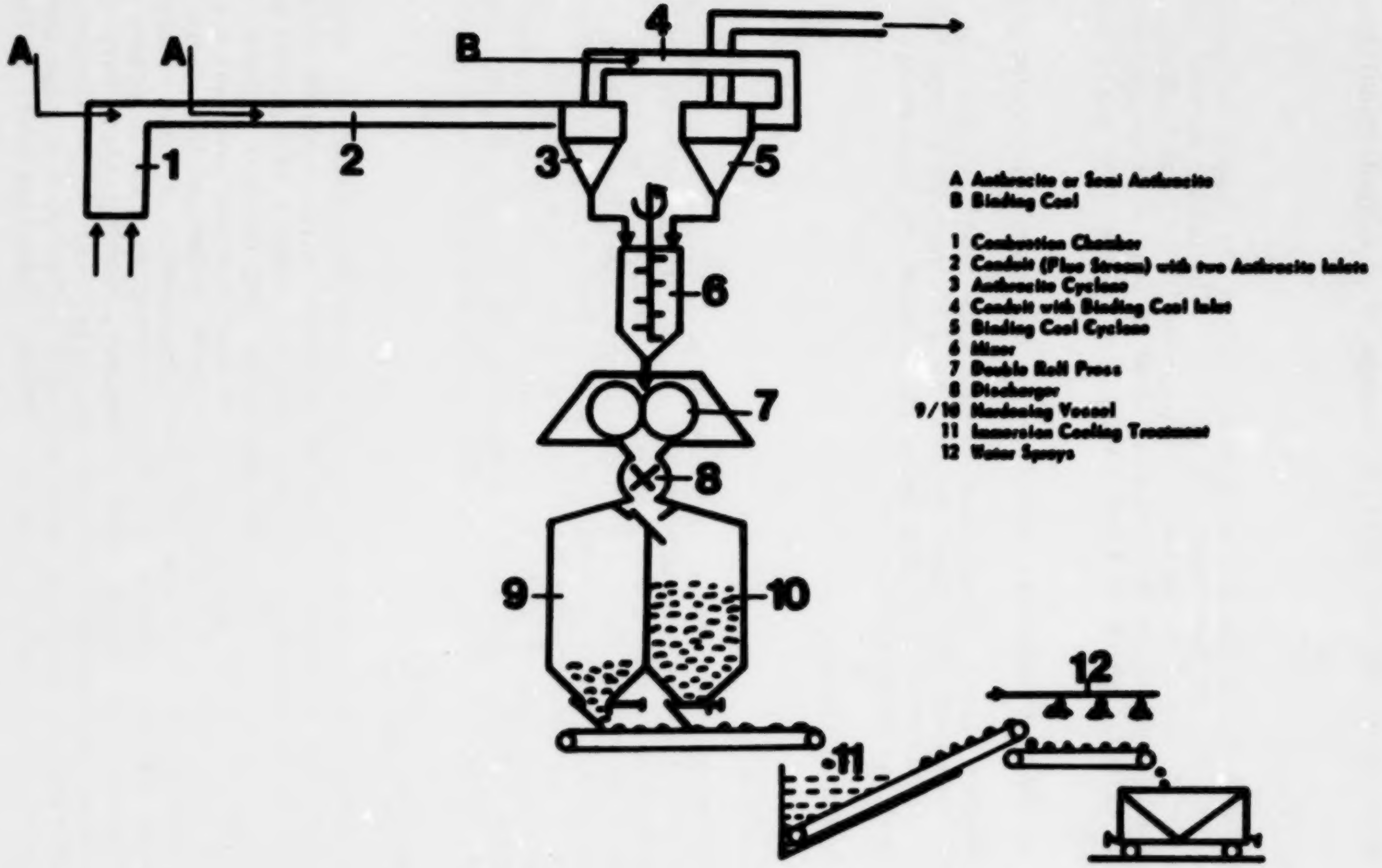

FIGURE 1 FLOWSHEET OF THE ANCIT FORMCOKING PROCESS

Two formcoke plants were built on the basis of the B.B.F. process - a 270 Mg/d plant at Prosper in Germany, and a 550 Mg/d plant at Scunthorpe, England. Both plants now are inactive because of process difficulties.

Coke Pellet Process

A second formcoke process being developed in the United States is the Coke Pellet Process, or the Consol-BNR process. The unique element of the process is the mixing of preheated coal, preheated char, and preheated pitch under controlled conditions in a rotating drum to form a sized agglomerate (snowballing effect), which is later calcined at an elevated temperature to produce coke.

Two of the more important objectives of the Coke Pellet Process are:

1. Produce strong, sized blast furnace coke from a single coal or from coal that cannot be used as a 100 percent charge to a conventional slot oven (due, for example, to unfavorable swelling properties).

2. Reduce pollution.

Clean Coke Process(2)

The Clean Coke Process is a development of United States Steel Corporation and, since 1973, has been developed under a joint project with the Office of Coal Research (now a part of the Department of Energy). The objective of this development is to permit the use of high sulfur, nonmetallurgical, high ash coals for cokemaking while producing low sulfur liquid and gaseous fuels as by-products in an environmentally acceptable manner. Estimates made for the case of processing 1 Mg of high ash, high sulfur Illinois coal indicate a yield of about 0.25 Mg coke, 0.12 Mg chemicals and 110 dm^3 of liquid fuel. The process, therefore, is much more than a formcoking process.

FMC Formcoke Process(1,3)

FMC started laboratory-scale work on a formcoking process in 1956. By 1958, the first few kilograms of coke were produced which appeared strong and useable. The basic concept of FMC was directed initially exclusively to the needs of their Pocatello, Idaho, phosphorus smelting furnaces. There, the high delivered cost of the small sized by-product merchant coke was a great incentive to such an effort. However, they soon recognized that their process also could benefit the steel industry; and consequently, a joint venture was formed between FMC and United States Steel Corporation. The objective was to build and operate a formcoking plant at Kemmerer, Wyoming, where very extensive coal reserves of subbituminous coal are available. This high moisture coal was regarded for years as excellent steam coal with rather poor storage characteristics because of its strong oxidizing properties. Extensive tests in the FMC laboratory and later at the 1 Mg/d FMC pilot facility at Philadelphia showed that this geologically young coal with absolutely no coking properties (in the conventional sense) yielded carbon agglomerates of apparently, satisfactory characteristics. The Philadelphia coke was first tested in Pocatello in 1959 and 1960 with excellent results.

The FMC process (Figure 2) utilizes the simple concept that coal having no agglutinating properties must first be brought to the level of carbon (char or calcinate) and then blended with binder and agglomerated to the desired shape and size.

In the FMC flowsheet, the coal is first crushed to (-3 mm), dried, pre-oxidized, and preheated in the first process step. The crucial carbonization step is carried out in the second fluidized bed vessel in which the previously preheated coal is partially devolatilized with steam and air. It is here that tars evolve which are later used for bonding the carbonaceous particles into a coke agglomerate. The discharge temperature from the carbonizing step reaches 480°C and the char, which is somewhat spheroidal in shape, moves to the third and last process vessel - the calciner, which operates at 870°C. Here the volatile matter is reduced from up to 17% to about 3%. Simultaneously, a shrinkage of the char particles is effected. The evolving low heating value gas (5.7 MJ/m^3) is used internally in the plant.

The calcinate, cooled to approximately 100°C, is thoroughly and intimately blended with a low temperature pitch binder produced from the raw coal tar and this blend is briquetted. The amount of the binder required varies between 8 to 15% by weight, depending on the characteristics of the calcinate. The briquettes are subsequently treated by first heating in an oxygen rich atmosphere to harden them and then devolatilized to a coke product containing about 2% V.M.

The Kemmerer, Wyoming, formcoke plant, built jointly by FMC and United States Steel, went on stream in 1961 and quickly started producing formcoke sized at 32 mm x 19 mm. In appearance, this plant resembles a chemical plant or a petroleum refinery and not a conventional coke plant. By the summer of 1962, a shipment of 1820 Mg of Kemmerer formcoke was tested in the United States Steel experimental blast furnace at Universal, Pa., with a 1.2 m diameter hearth. The formcoke performance was compared with that of Gary by-product coke sized in two ranges: small coke 19 mm x 5 mm, and large coke 32 mm x 19 mm.

The furnace experienced very few problems, and for the duration of the test, the Gary by-product coke and the FMC coke were easily interchanged.

In 1966, an agreement was reached between Armco steel, Inland Steel, and the FMC to carry out the first test with formcoke on an Armco commercial blast furnace at Hamilton, Ohio.

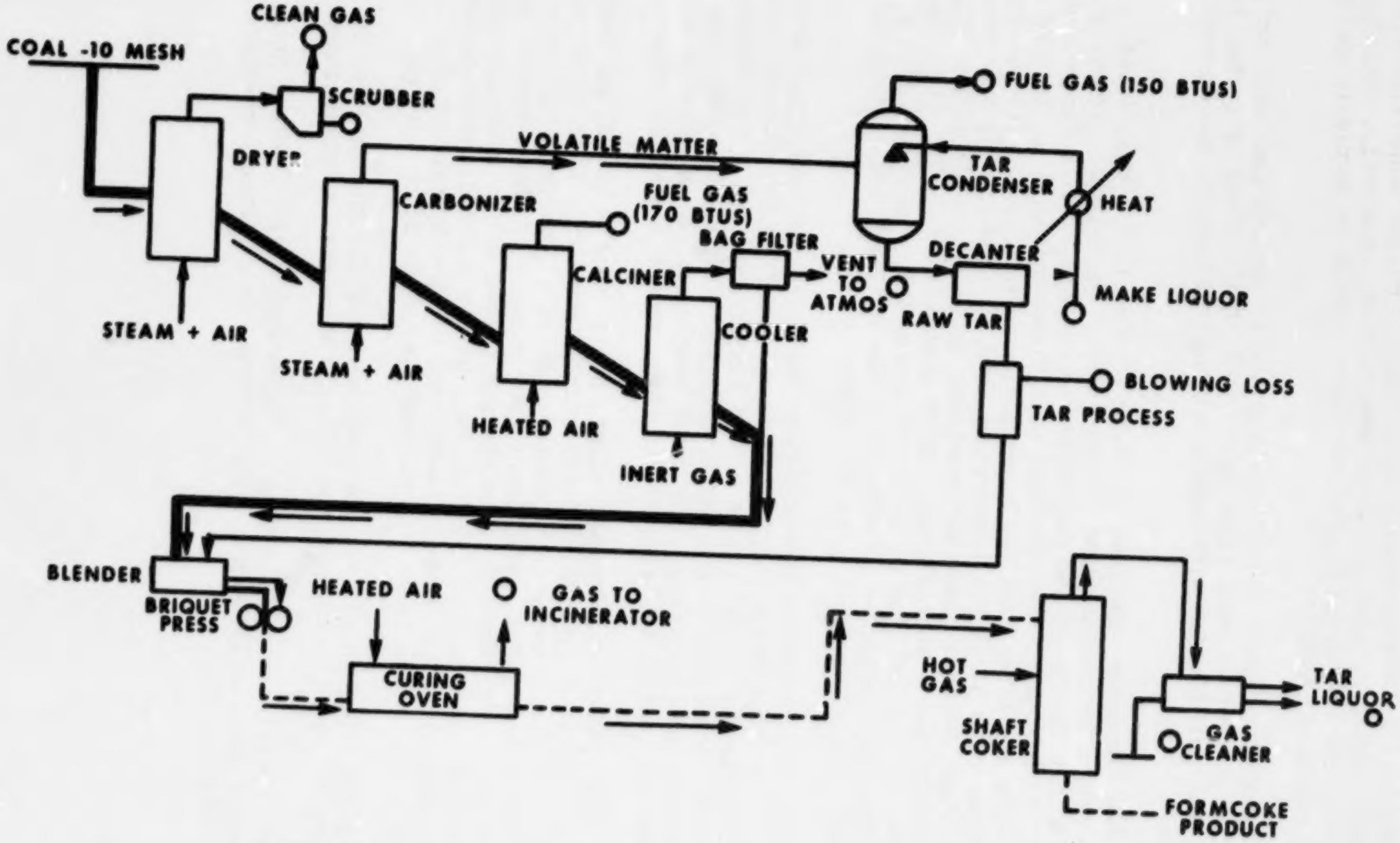

FIGURE 2 FLOWSHEET OF THE FMC FORMCOKE PROCESS

First, a preliminary test with 500 Mg of 35 mm briquettes was conducted in October, 1966. The problem of coke fines, which were generated in handling, was noticed but it appeared that the quality of the briquettes being produced for the test could be improved. In the spring of 1967, 11,700 Mg of 50 mm formcoke pillow briquettes and about 1,300 Mg of 35 mm pillow briquettes were shipped to Armco's blast furnaces at Hamilton, Ohio. The program was to replace 100% of the furnace coke as soon as possible using a stepwise approach.

After a short period at 50% replacement with 50 mm formcoke in the burden, the furnace operation became erratic; the furnace went cold, slipped, and filled the tuyeres and blowpipes with slag. During the test, as compared to a normal operating period, the production rate decreased by about 35%, and the furnace operation was erratic. On the basis of flue dust analyses, it was estimated that about 110 kg of formcoke fines were blown out per each Mg of hot metal produced.

The Armco-Inland-FMC test was obviously somewhat of a disappointment. However, it must be borne in mind that in this test, large 50 mm briquettes were used extensively for the first time. The test was conducted without knowledge of what to expect from this new coke and what properties to demand. The results strongly indicated that the coke must be structurally strong and abrasion resistant.

In October of 1970, FMC and Inland Steel undertook a joint study to determine the feasibility of producing formcoke from No. 6 Illinois coal in the Kemmerer plant. For this purpose, 820 Mg of Illinois coal were shipped to Wyoming and processed into 38 mm formcoke briquettes in September of that year. It was found that the Illinois coal could be used quite easily if it were properly preoxidized in the first process step of the FMC process.

To help control the surface abrasion, the finished coke flowing from the loadout bin into the railroad car was sprayed with a solution of calcium lignosulfonate, which appeared to easily soak into the briquettes. A total of three cars of Illinois formcoke were received at the Indiana Harbor blast furnaces, of which two were treated with lignosulfonate and one was left untreated. The unloading of these cars into highline bins showed that the treated formcoke generated very little airborne dust, particularly when water was sprayed during the unloading operation. The untreated car was quite dusty.

The lignosulfonate treatment was obviously not the only improvement which affected the quality of the resulting Kemmerer briquettes. Changes which greatly influenced the structure of the briquettes were made in the plant operating practices and a large scale test on an intermediate size, well operated blast furnace was considered.

At about this same time, the British Steel Company and FMC agreed on the production of 2,730 Mg of FMC formcoke made of Kemmerer coal, which would be subsequently shipped to England for testing at the East Moors Blast Furnace No. 3(4). The formcoke sized 38 mm x 38 mm x 25 mm was shipped in stages with transfer points at St. Louis, New Orleans, Barry near Cardiff, and finally East Moors.

The conclusion reached by the British Steel Corporation can be summarized as follows:

1. The shipment of FMC formcoke, which was treated with lignosulfonate, was not hampered by dust problems and breakage, despite the numerous transfer points and the distance (about 10,500 km).

2. This trial established beyond all reasonable doubt that calcine based formcoke could replace a superior quality conventional coke at the 100% level with improvements in efficiency and at potentially higher production levels.

Consortium Test

In the spring of 1973, a consortium of five steel companies and FMC was formed to conduct a large scale blast furnace test with FMC formcoke. These included Armco Steel Corp., J&L Steel Corp., Inland Steel Company, McLouth Steel Co., and U. S. Steel Corporation.

The detailed information developed during the total test program with almost 18,200 Mg of coke has been presented elsewhere(5). However, in summary, results were as follows:

1. The shipment, storing, reclaiming, and handling of the 50 mm formcoke to the plant and in the blast furnace charging system presented no difficulties.

2. The furnace operation was found to be normal when up to about 50 percent FMC coke was used. At high levels of substitution, increasing instability of operation was noted, which was attributed to factors related to the materials distribution pattern within the furnace.

Because of the limited quantity of formcoke available for the test, development of operating practices to achieve stable operation at formcoke substitution levels up to 100% was not possible. Inland Steel concluded that the experimentation required a formcoke production plant with a production rate that would be in balance with an operating blast furnace. Thus, to advance the technology, Inland Steel, in 1978, retained Davy McKee to conduct a preliminary engineering study of a 910 Mg/d formcoke production plant. The results of this study were used as a basis for an unsolicited proposal to the Department of Energy for a cooperative agreement to conduct the Inland Steel Formcoke Demonstration Project. This proposal was submitted in April, 1979, and is currently being considered by DOE.

ENVIRONMENTAL ADVANTAGES OF THE FMC FORMCOKE PROCESS

The emission-control problems associated with conventional coking operations have been well documented and are only too apparent to all of us who have striven over the years to improve on coke battery pollution abatement. The great difficulties which we have experienced in controlling battery emissions are caused by the complexity of operations inherent to batch production of coke.

We won't attempt to review those operations in any great detail, but it may suffice to say that the charging, coking, pushing and quenching steps associated with operating multiple-slot oven batteries create a great number of potential sources of emissions. For example, a typical coke battery might consist of 87 ovens which--in one complete operating cycle of from 12 to 24 hours--requires at a minimum, opening and closing 174 doors, 435 topside lids, 87 standpipe lids, to say nothing of maintaining seals on these closures during the actual coking period. Recognizing that a coke battery constructed of large quantities of brick is subjected to considerable thermal stress during its lifetime, which exacerbates the leakage problem, it is no wonder that pollution abatement requires an intensive round-the-clock maintenance effort. Even when emissions are minimized, the major problem remains of collecting or capturing these emissions where possible from the multiple sources for subsequent removal in pollution abatement equipment. While great strides have been made to date, coke batteries remain one of the toughest problem areas and the last to yield to innovative technology. The best equipment and practices available today simply cannot prevent intermittent emissions from coke oven batteries.

The FMC formcoke process, by its very conception as a continuous production sequence, offers excellent opportunities to reduce emissions. The coal feed is processed continuously in fluid bed reaction vessels which isolate the coal from the atmosphere. As can be seen in the formcoke flowsheet in Figure 3, the coal once fed into the first fluid bed vessel is not exposed to the atmosphere until it exists as calcined char which is mixed with binder and briquetted at midstream of the process. The green briquettes enter again an enclosed processing equipment and reappear as cooled coke briquettes being delivered to the storage silo. All of the process vessels are made from continuous steel shells, rather than the nonmonolithic masonry in conventional coke batteries.

Prevention and repair of leaks in steel casings are relatively simple. The vessels are not routinely opened and closed as an integral part of the production process, therefore, there are no charging, door, topside, pushing or quenching emissions characteristic of slot coke oven batteries.

As a result of: 1) the Inland-Davy McKee Engineering study; 2) the proposal evaluations conducted for DOE by The Ralph M. Parsons Company(6) and for the Environmental Protection Agency by Research Triangle Institute(7); and 3) data obtained from the FMC Kemmerer, Wyoming formcoke plant, considerable information regarding the environmental aspect of the FMC formcoke process are now available.

To control airborne emissions from an FMC formcoke facility, we would expect to install LAER (lowest achievable emission rate) technology for a new facility on the few point sources which exist and BAT (Best Available Technology) to control waterborne pollutants. The present process as shown in Figure 3 indicates the following pollution controls:

1. Coal handling and preparation is a separate step in the Inland Formcoke configuration. Gases and dust off the coal dryer are scrubbed prior to discharge.

2. A front end incinerator would combust emissions from:

   (a) the catalyzer
   (b) the briquetting step
   (c) the curing oven, and
   (d) the binder preparation area

   Cyclonic separators and scrubbing equipment would precede or follow the incinerator as required. In addition to controlling process emissions, the incinerator would furnish the inert gas required in the process.

3. The off-gases from the Carbonizer and the Calciner which contain coal fines in addition to volatile organic compounds distilled from the coal are stripped in cyclones, venturi scrubbers, wash towers and electrostatic precipitators as required. The tar removed in this sequence is sent to the binder preparation plant. The off-gases are combined and after steps to remove naphthalene, ammonia and light oils (not shown) sulfur is removed in a desulfurization step--possibly a Stretford unit as shown. The desulfurized gas is used to generate steam in a boiler for use throughout the steel plant.

4. A fabric filter serves the calcinate storage silo to remove fine dust. This material can likely be added to the subsequent mixer step prior to the briquetter and thus recycled.

5. Emissions from the Briquette Curing Oven contain dust and some volatiles and are combusted in the front end incinerator as previously mentioned.

6. Off-gas from the coking kiln passes through a cyclone, venturi scrubber and an electrostatic precipitator to remove dust and tar. The tar is returned to the binder preparation plant. Some of this low Btu off-gas is returned to fuel the kiln, whereas, the rest is sent through its own desulfurizing step. The resulting clean kiln gas is then used as fuel in the curing oven and the coal dryer.

7. Fugitive emissions from the briquette screening step and from the handling and distribution steps are removed in cyclonic separators or fabric filter as required. The dust is recycled back to the mixer preceding the briquetter

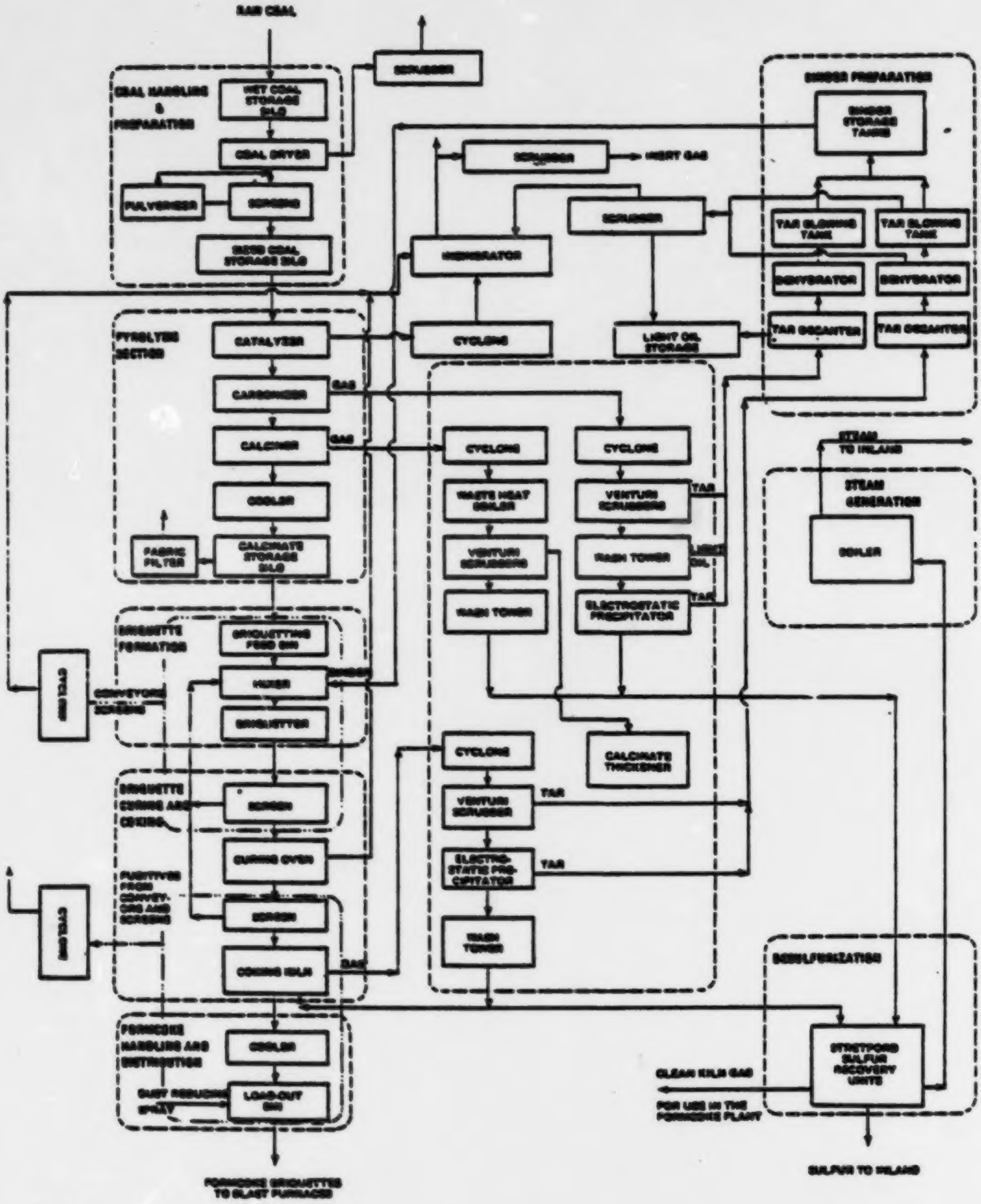

FIGURE 3 PROCESS FLOW DIAGRAM FOR PROPOSED FORMCOKE DEMONSTRATION PLANT

8. Generally, all scrubber liquor would be recycled after solids removal in the calcinate thickener. The sludge could be dried and recycled back into the process or combusted in a separate system. Blowdown from the system would be physically-chemically treated to remove the small quantities of cyanide and ammonia prior to biological treatment.

In addition to the pollution control that can be achieved with the FMC formcoke process, recent tests at the FMC Kemmerer plant established that the plant is in compliance with the 1978 OSHA emission standards controlling coke oven worker exposure(8). The results indicated no worker was exposed to ambient air Benzene Soluble Fraction of Total Particulate Matter (BSFTPM) concentration as high as the OSHA limit of 150 $\mu g/m^3$.

In summary, the environmental and health/safety advantages of the FMC formcoke process are considerable and, while specific emission and effluent limits have not been set, we are confident that they can be met and at a cost substantially below that for conventional batteries. This would include the abatement equipment, labor and repair requirements and energy consumption.

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FUTURE STEEL TECHNOLOGY AND THE ENVIRONMENT

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ABSTRACT

According to the OTA report TECHNOLOGY AND STEEL INDUSTRY COMPETITIVENESS, there are considerable opportunities for major new steelmaking technologies to be created and introduced in the domestic steel industry during the coming decades. During the decade of the 1980's there will be continued increases in the use of scrap based electric furnace steelmaking by both nonintegrated and integrated steelmakers. Moreover, there will be substantial increases in the use of continuous casting of steel. One of the important impacts of these changes will be the need to use direct reduced iron as a complement to ferrous scrap in electric steelmaking furnaces. The shift to greater scrap use and the gradually increasing use of direct reduced iron signifies less dependence on ironmaking in blast furnaces fueled primarily by coke. Thus, pollution should be abated. Although there may be very limited introduction of coal based direct reduction during the 1980's in the United States, in the 1990's we may see large scale direct reduction plants based on coal gasification and more DR plants using coal directly. Federal policies shape the development and use of new technology. Those policies that aid and reward the companies with the poorest performance may be detrimental to a competitive domestic steel industry, such is the nature of President Carter's proposal to grant extensions to the compliance schedule for the Clean Air Act to certain qualifying plants.

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FUTURE STEEL TECHNOLOGY AND THE ENVIRONMENT

In his recently announced program[1] for the domestic steel industry, President Carter linked the goals of modernization and environmental protection in a more precise manner than ever before. The key proposal is an amendment to the reauthorization of the Clean Air Act which would allow the EPA Administrator to use discretion, on a case-by-case basis, for extending by up to three years the deadline for compliance with the requirements of the Act. A number of conditions must be met, with the key point being the requirement to modernize existing steel facilities with the funds that would have been spent to meet the original compliance schedule. Also included in this policy package for the steel industry is the acceptance of greater use of the "bubble concept" and the stabilization of discharge permits under the Clean Water Act until EPA's revised regulations take effect in 1981. How will changing steelmaking technology affect the environment, and how will these policy changes affect the introduction of new technology in the domestic steel industry? These are the key issues I would like to explore.

How Much of a Problem Have Environmental Regulations Been for the Industry?

The premise behind the new policy thinking described above is that compliance with environmental regulations is costly. As President Carter has said, "Full compliance will require large additional expenditures at the very time that the industry must also make major investments for modernization."[1] The implication is that the industry cannot do both modernization and compliance at the same time for all steelmaking facilities. Just how easy a case can be made by companies for specific facilities for extension of the compliance schedule is not entirely clear. But based on the strong positions taken by individual companies and the American Iron and Steel Institute that insufficient profitability and capital formation have been debilitating, there is some indication that past industry interpretations of their financial problems will continue, and that many requests for compliance stretchouts would be made. To what extent have past environmental regulatory costs been a severe burden to the industry and an obstacle to modernization?

During the period 1971 to 1978 pollution abatement capital expenditures equaled 14.5% of total capital spending for the domestic steel industry according to AISI data. In that same period, using data from the same source, spending on non-steel investments (diversification) amounted to 16.0% of total capital spending.[2] Both diversification and reinvestment strategies have been used successfully and unsuccessfully to increase profitability. However, regulatory compliance investments have not been sufficiently large to prevent diversification when that was desired, nor have the considerable diversification efforts of the past decade brought about any remarkable improvement in steel industry profitability. Moreover, the industry has maintained paying relatively high dividends to its stockholders, regardless of the generally low profitability it has usually had. During this same period of 1971 to 1978 dividends amounted to 46% of net income and was equivalent to 23.9% of total capital spending. There is, of course, a responsibility to make a return on stockholders investments as well as to the public to maintain a clean environment. Nevertheless, steel industry management have perpetuated a climate in which the value of owning stock in most large steel companies is based on current return rather than on appreciation of the stock which is hinged to perceptions of future success. Both dividends and non-steel investments are discretionary uses of available capital, and it is, perhaps, an ethical issue and a question of values as well as anything else as to whether these uses have priority over the corporate responsibility to refrain from polluting the environment.

Certainly, diversification is a rightful perogative of corporate managers, but interestingly Hall's recent study of eight mature domestic industries, including steel, revealed that diversification has not been successful because: "By waiting too long to begin diversification efforts, most lack the capital and managerial skills to enter new markets and/or to grow businesses successfully in these markets. Thus their diversification efforts to date have been too small or have been managed in too conservative a fashion to obtain sustainable performance improvements, as witnessed by the very minor performance contribution of U.S. Steel's diversification program into chemicals..."[3] The exception for the steel industry has been Armco, the most diversified and profitable "steel company", which used a strategy of investment in low cost steel production in selected regional segments as well as early and well managed diversification. And it has been Armco which has lead the effort to use the "bubble concept" to economically meet emission standards for nontoxic pollutants.

Since the domestic steel industry makes much importance over comparisons between itself and the Japanese steel industry, it is interesting to note how to Japanese have responded to the social demands for a clean environment. During the period from 1971 to 1978 the Japanese spent 13.4% of their total capital spending on pollution abatement. Although this is slightly more than what the domestic industry spent as a fraction of total capital spending, it does not fully capture the difference between the industries. By normalizing actual pollution abatement spending on the basis of the amount of raw steel produced during this period, it is possible to see that the Japanese have had a greater intensity of spending. The per ton (metric) capital spending on pollution abatement during this period was 50% greater for the Japanese as compared to domestic spending.[4] This was true even though the Japanese had the advantage of new plant construction, for the most part, as compared to retrofitting in the United States.

The Japanese have put much effort into pollution abatement technology because Japanese ambient air quality standards are generally more stringent than those in the United States. For example, the 24 hour SO_2 standard in Japan is 0.04 ppm, as compared to 0.14 ppm in the United States, the one hour standard for photochemical oxidants is 0.06 ppm in Japan and 0.12 ppm domestically, and the standard for particulate matter in Japan for 24 hours is 100 $\mu g/M^3$ and 260 $\mu g/M^3$ for the United States.[5]

There is no denying the reality that compliance with environmental regulations has been expensive for the domestic steel industry. However, it can only be viewed as a contributory factor to the industry's problems. By itself, regulatory spending cannot explain the industry's declining profitability. Thus, while Federal policies aimed at reducing the costs of compliance are useful and appropriate - if they do not also lead to significant health threats to the public and the workers of the industry - they are not likely going to lead to some swift or meaningful turnabout in the performance of the industry in general, or of the companies and facilities with the poorest technological and economic performance.

One factor generally overlooked when considering the burden of complying with environmental regulations is the substantial use of Industrial Development Bonds. Such financing reduces the need for internally generated capital and makes large amounts of outside funds available at low cost and for long periods of time. Since State and local governments make tax-exempt revenue bonds available to companies, this is a form of public subsidy for what is reasoned rightfully to be a public good. During the past decade the domestic steel industry has used IDB's to generate nearly half the capital requirements for pollution abatement investments.[6]

In the AISI analysis of what the domestic steel industry's capital needs are for the next decade, the money needed for regulatory compliance ($800 million annually in 1978$) represents 12.3% of the total, the same as the fraction designated for diversification efforts. In actual fact $700 million of this is for pollution abatement (10.8% of the total) and $100 million is for meeting OSHA regulations. An EPA analysis forecasts about $500 million annually to meet pollution control needs during this period.[7] Thus, with the likely lower level of environmental spending, diversification would outweight regulatory compliance.

Trends and Prospects for New Technology

During the past decade there have been two trends which undoubtedly will continue and which reduce pollution. These are the greater adoption of electric furnace steelmaking and the use of continuous casting.

The fraction of steel made in electric furnaces rose from about 15% to 25% during the decade of the 1970's. The greater use of domestic ferrous scrap in electric furnaces signifies that less primary ironmaking in blast furnaces and less cokemaking are going on. This shift form integrated to nonintegrated steelmaking reduces pollution and the costs of pollution abatement substantially. Although there are limits to both the total amount of ferrous scrap available and to the amount of high quality scrap, there will be a continued increase in electric furnace steelmaking, probably to the 35% to 40% level in the 1980's.

The second most important trend is the greater use of the highly efficient continuous casting method of converting molten steel into solid shapes rather than the multiple step ingot casting approach. Continuous casting reduces pollution directly because of the elimination of soaking pits and furnaces, and indirectly because of the substantial increase in yield of the process. The increase in yield means that more finished steel is produced from a given amount of raw steel, usually in the order of 10% to 15% more finished steel. This means that less steel and less iron has to be made and thus pollution is reduced. During the past decade domestic use of continuous casting, although low compared to most other industries, has increased dramatically from just a few percent to over 15%. By the end of the decade it should approach 40% to 50%. Modernization of existing plants will be based on retrofitting existing facilities with continuous casting to a large degree because the many benefits of continuous casting, including reduced energy consumption, lead to return on investments of over 20%, and even more for alloy and specialty steels.

Both electric furnace steelmaking and continuous casting are well proven technologies. Considerable attention, both here and abroad, is being given to the development of truly new technologies that must be proven technically and economically on a pilot and demonstration level first. According to the recently completed study of the domestic steel industry by the Office of Technology Assessment, the most important new technology for the domestic steel industry during the next several decades will be coal based direct reduction. Unlike natural gas based direct reduction which is undergoing phenomenal expansion throughout the world, coal based direct reduction has been used in only a few places in relatively small operations. Newer forms of direct reduction that can use cheap grades of coal and possibly coal gasification to produce either conventional direct reduced iron (DRI) or molten iron are being developed.

For the United States with abundant supplies of low grade coals, the prospect of coal based direct reduction offers a number of potential advantages. Capital and operating costs may be substantially lower than the blast furnace and coke oven route once the technology is fully developed. Most coal DR technologies are relatively simple, one step processes that offer a closed system approach with very little pollution. Moreover, like natural gas based direct reduction, a modular rather than economy of scale approach can be used. For the cyclic steel industry with capital problems as well as considerable uncertainties for demand, foreign competition and government policies, the ability to construct relatively small coal DR modules is most attractive.

Since the increasing use of electric furnaces will put much pressure on ferrous scrap supplies, in terms of quantity and quality, there will be an increasing need for direct reduced iron to be used as a complement to scrap. Although DRI is already becoming a world traded commodity because of the rapidly increasing DR capacity in natural gas rich nations, such as Mexico, Venezuela and Saudi Arabia, other factors are likely to make domestic DR plants economically viable. During the 1980's we will likely see several different coal based DR technologies both proven and adopted in the United States on a small scale, possibly at nonintegrated steel mills or as merchant DR plants serving a geographical region with limited ferrous scrap availability and a relatively high rate of growth in steel consumption. During the 1990's it is quite conceivable that larger scale coal gasification DR plants will be constructed. The integrated plant of the future may be based on DR rather than the blast furnace.

Critics of DR rightfully note that at present large scale DR plants could not be justified. However, it is crucial to understand that coal DR technology is in its infancy and that many improvements are likely to result from the substantial amount of R&D activity in this area. The two most important driving forces for developing coal DR technology are the reductions in capital costs and pollution. Creating and adopting new technology is facilitated by both rapid company growth and profitability. In the United States there is a segment of the domestic steel industry which satisfies these conditions. This is the nonintegrated segment, the scrap based minimills, midimills or market mills which have undergone tremendous growth in the past decade, from only a few percent of the domestic market to about 15% today. The OTA study forecasts that by 1990 these companies could account for at least 25% of the market. Since the growth of these companies must depend on broadening the product mix to include higher quality steels, the need to introduce virgin iron in the form of DRI will be critical. And many of these companies have already demonstrated their inclination and ability to innovate quickly in new technology. Even with the increased capital costs of constructing DR facilities, the total capital costs for combined DRI-scrap based mills could be less than the costs for a conventional greenfield integrated plant or even the costs for extensive modernization of existing integrated plants. For example, according to the OTA study, the capital costs of a combined DR-scrap plant would likely be approximately $500 per metric ton of annual steel product capacity, about one third that for a conventional greenfield integrated plant.

A number of other major changes in technology are likely to be developed commercially within the next decade, these include: formcoking, plasma steelmaking, direct casting and a host of relatively incremental technical improvements which when applied collectively to a particular plant represent a substantial overall improvement in efficiency. Virtually of these changes imply reductions in pollution because they make use of closed systems and reduce the dependence on conventional cokemaking, either directly or indirectly by improving efficiency and yield in the steelmaking portion of the mill.

Contrary to some concepts popularized about the steel industry, iron and steelmaking technology is far from static. Technology is a problem solving tool that bold and risk taking managers can use to deal with problems of limited capital availability, rising labor costs, environmental regulations and raw material constraints. Future steel demand is uncertain and any increase in demand will be small. Nevertheless, steel will remain an absolutely critical material for all societies. Recent oversupply conditions have taught valuable lessons to most steel industries, particularly those in Europe. There is a good possibility of a close match between world steel supply and demand leading to higher profits in the mid-1980's. It is this perception by many people both in the industry now and examining the industry from afar that is stimulating the development of new technologies, particularly those such as direct reduction that will make entry into the industry easier. All these changes, including the influx of increasing amounts of foreign capital into the domestic steel industry, will likely lead to reduced environmental pollution in the years ahead.

Federal Policies Affect Modernization

Although Federal policies concerned with the environment may relieve some of the immediate problems of capital availability, they are not likely to serve as a major stimulus for modernization based on the most innovative technologies or for modernization of plants which are already relatively efficient.

Policies which more directly deal with capital formation, RD&D, and prices have greater ability to influence modernization based on new technology. With the exception of the growing nonintegrated segment of the industry and the highly efficient and competitive alloy/specialty steelmakers, the absence of a coordinated set of policies for the steel industry which leads to a substantial increase in profitability for the large integrated companies will likely result in the continued contraction of this segment of the industry. If the nonintegrated segment can compensate for the loss in capacity of the integrated companies, or even if greater levels of imports result, the net effect for the nation will be reduced pollution. There are, of course, a number of undesirable side effects of increased imports, including loss of employment and a threat to our national security should imports rise above about 20% of domestic consumption.

The important issue is not how to reduce pollution by reducing domestic steelmaking capacity and increasing our dependence on foreign steel. It is how do we both decrease pollution and maintain competitive and profitable steelmaking capacity. The key here is a combination of Federal policies and changes in the industry itself which lead to the greatest use of the most innovative technology by the best managed companies rather than policies which tend to protect the poorest managed and performing companies.

If one object were to insure a viable competitive steel industry, then the President's idea of three year extensions for some plants could aid the wrong facilities, and the companies that have delayed compliance and modernization could be rewarded. There are, after all, a number of old inefficient and poorly located steel mills that are not truly competitive. The spectre of concentrated losses of jobs from plant closings could be dealt with by appropriate worker retraining and relocation programs. Like other policies, such as the recent EDA loan guarantee program, this regulatory approach tends to give advantage to those firms with the least competitiveness, rather than rewarding those better managed companies that would benefit from incentives for still greater risk taking and investments in the future. Greater application of the bubble concept appears to be a more acceptable approach to meeting the objectives of reduced pollution and freeing more money for modernization by companies.

The skewing of competitiveness by Federal policy is illustrated by the situation of Inland, Bethlehem and U.S. Steel, all with large integrated plants in the Chicago region. By investing in steelmaking, using innovative technology and having good strategic planning and management, Inland became the lowest cost domestic producer (or large integrated steelmakers) and reduced their pollution. But Bethlehem and U.S. Steel plants serving the same market are far less efficient and, if President Carter's proposal is accepted by Congress, they could use capital to invest in modernization rather than pollution abatement at a time when they will receive even greater tax benefits from modernization capital investment than Inland did some time ago. Interestingly, the extension proposal asks only that "funds which would have been spent to comply with the deadline will be expended in the same time period for modernization," but there is little indication that such a level of spending would normally be sufficient to modernize qualifying plants to a significant degree. Moreover, the maximum of three years for extension is not long enough to plan and implement major forms of modernization. Cash flow from such plants could still be used for diversification out of steelmaking. Federal policy, such as the three year extension, therefore, gives Inland's higher cost competitors an advantage, but in the long run it cannot make these less efficient and more poorly managed plants independently competitive.

Moreover, Federal policies need more comprehensiveness. For example, although modernization is a worthy goal and new technologies may indeed reduce air and water pollution, we know that in many cases the pollution will merely be shifted to the solid waste category. The proposed policies may demonstrate to companies that they are better off in the long term by fighting compliance with RCRA and the regulations affecting hazardous wastes, and by using available capital for purposes such as diversification.

What is needed are incentives for developing, testing and adopting new technologies that offer less pollution of any kind (including noise for example) together with sufficient economic benefits to justify private investment. Rather than tying delayed spending on compliance to modernization, it may be useful to consider linking it to high risk R&D on innovative steelmaking (including pilot and demonstration activities). Two reasons support this point of view. First, the level of R&D spending by the industry as a whole and by individual companies is closer to the level of spending on compliance with environmental regulations; that is, hundreds of millions of dollars annually for the industry for both cases, rather than billions of dollars needed every year for capital spending on modernization. Thus, the impact would be reater on R&D than on modernization. Second, as the OTA study showed, a relationship between environmental capital spending and R&D spending exists for the past decade. For example, from 1969 to 1973 the average ratio of R&D to environmental capital spending was unity, but from 1974 to 1978 the average ratio dropped to one-half. The increase in environmental capital spending from the earlier period to the later one was from an average of $157 million to $440 million annually. Environmental capital spending appears to be influencing the discretionary use of corporate funds on R&D in the domestic steel industry. R&D spending is not linked to total capital spending by the industry.

This policy approach of fostering R&D rather than modernization appears to have the disadvantage of shifting the use of funds from the plant to corporate level. However, by promoting intrinsically profitable, efficient and clean technology, it has the potential to foster legitimate, long term industry competitiveness. Using the bubble approach to deal with short term needs and the freeing of capital for modernization, and the compliance schedule extension for supporting long term R&D, federal policies could help the domestic steel industry in a fair and comprehensive manner.

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Session 1: AIR POLLUTION ABATEMENT

Chairman: Thomas J. Maslany
Region III
U.S. Environmental Protection Agency
Philadelphia, PA

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Title: A MODEL FOR COKE OVEN CHARGING EMISSIONS

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Abstract: This paper discusses coke oven charging emissions from well controlled coke oven batteries. They are found to follow a statistical distribution that is badly skewed toward long times, although the mode and mean times are short. Causes of occasional long emission times are explained. It is suggested that charging emission standards of the type that permit a limit of L seconds visible emission per N charges, such as 125 seconds per five charges, will inevitably be violated and are inappropriate. The paper suggests that the standard should be a limit on per cent of visible charge emissions exceeding 25 seconds. The limit should depend on battery age and features. The paper suggests compliance be determined from an average derived from a month or more of observations.

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A MODEL FOR COKE OVEN CHARGING EMISSIONS

I. Introduction

The author has participated in several dialogues of the following type:

Agency Person:	"The standard for coke oven charging emission should not exceed 125 seconds for five successive charges."
Industry Rep:	"That is too strict. It can't be done."
Agency Person:	"It is being done and it is actually a generous standard. We have data to show batteries meeting 35 seconds for five charges."
Industry Rep:	"But you ignored other data that showed the same battery exceeding 125 seconds for five charges."
Agency Person:	"That was because of equipment breakdown or human error."
Industry Rep:	"But there are always breakdowns and human errors at coke ovens."

The participants in this dialogue are looking at the same animal from two different perspectives and are focusing on two different extremes of its possible behavior. I believe the divergence in viewpoint stems from the two parties having different "models", if you will, of the behavior of coke oven charging emissions. I believe the way to progress toward the goal of an equitable standard for coke oven charging emission performance will be to first find the right model, one that faithfully describes its behavior. Then one can determine useful things about measuring and controlling coke oven charging emissions.

II. Data

A. Data Sources

I have collected data on visible emissions during charging from ten different batteries operated by five different steel companies in five different geographic areas. This was not a random sample. These are not average coke batteries from the standpoint of charging emission control. Nine of the ten were the best performing batteries out of an aggregate of about 90 coke batteries collectively owned by their companies. The tenth battery is an old one which was included to give some perspective to the performance of the other nine. Most of this data was measurements of charging emissions made on a self-monitoring basis by representatives of the individual companies (not necessarily the battery operators) who were required to submit monthly or quarterly reports to state or local agencies. I don't believe there was any tendency to overemphasize long emission times because these reports of long emission times are self-reported failures to meet regulatory requirements. I picked batteries where much effort has gone into equipping the batteries properly and training the operators to perform good stage charging. Among these are two which U.S. EPA describes as "exemplary" for stage charging control. Several others come very close to the exemplary batteries in their performance. One old battery does not. Even this old battery performs better on charging emissions than many others, including some much newer batteries. In this paper I have called them batteries 1, 2, 3, . . . 10. (See Table I).

Table I - Battery Characteristics

	Height Meters	Collecting Mains	Period Observed	Notes
Battery 1	4	1	9/12/79 to 4/2/80	
Battery 2	3½	1	11/1/79 to 6/30/80	
Battery 3	3½	1	11/1/79 to 6/30/80	
Battery 4	6	2	11/1/79 to 6/30/80	
Battery 5	4	1	11/1/79 to 6/30/80	
Battery 6	4	2	6/1/79 to 11/30/79	(1)
Battery 7	4	1	1/1/77 to 2/12/80	(2)
Battery 8	3½	2	1/1/80 to 4/30/80	
Battery 9	3½	2	1/1/80 to 4/30/80	(1)
Battery 10	3½	2	1/1/80 to 4/30/80	

(1) Battery described by EPA as "exemplary" for charging emissions

(2) Battery 7 is more than 35 years old

B. Histograms and Cumulative Frequency Plots

I have plotted two types of histograms of the charging emission times. When data on individual charges were provided, (all batteries except No. 6), I plotted histograms of individual charge times (see Figure I). For example, in Figure I the histogram for Battery 1 is constructed from 745 observations of individual oven charges. When data were available as cumulative time, i.e., emission time cumulated from four to seven successive charges, I plotted histograms of average charge time (see Figure II). For example, in Figure II the histogram for Battery 1 is constructed from 149 averages of the cumulated sum of emissions from five successive charges. Therefore, Figure II is arrived at as if 149 compliance tests had been performed at that battery. Also I plotted the individual oven charge emission data on a cumulative frequency plot where the per cent of observations less than a certain time is plotted on a normal probability scale against the logarithm of the time (see Figure III).

C. Characteristics of the Histograms

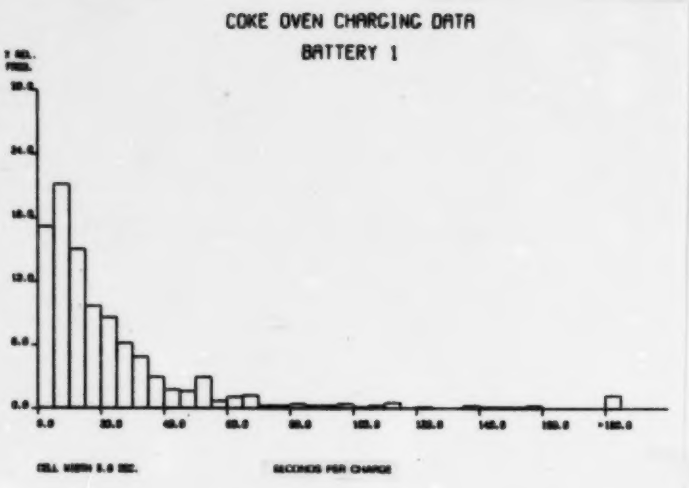
Each battery has its own unique histogram. However, as a class, the histograms have common features. They are badly skewed distributions with the skew toward the long time. The mode and mean times are short, mainly in the range of 5 to 25 seconds in the individual charge histograms. However, each of the batteries produced some very lengthy times exceeding ten times the mean. In the average time histograms the distribution is not as badly skewed because the cumulation of four to seven consecutive emission times tends to average longer and shorter times. Even so, on each battery there are a few observations that exceed four times the mean.

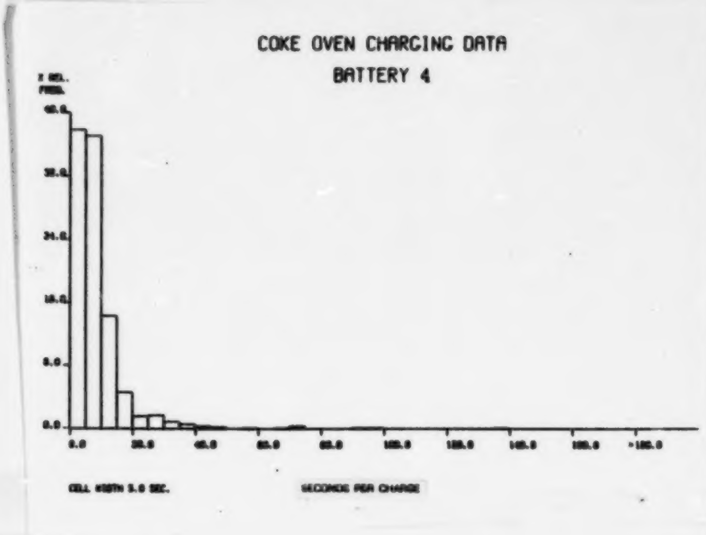
D. Characteristics of the Cumulative Frequency Plots

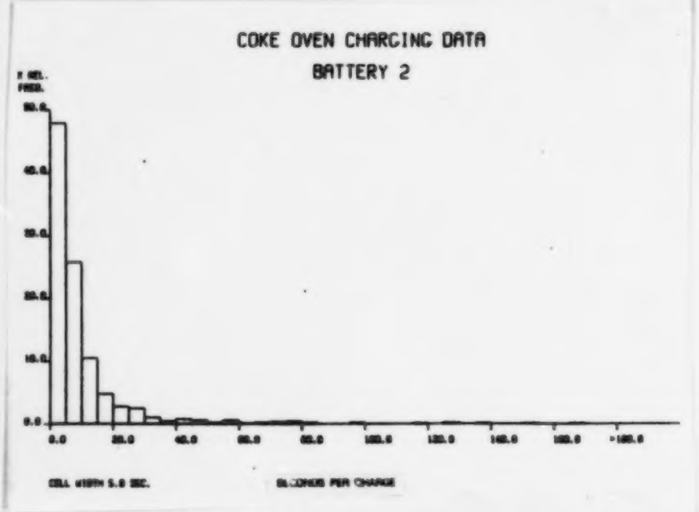
In Figure III the data from all the batteries seemed to be reasonably representable by a straight line. However, each battery has its own line and the slopes of the lines are not all equal. Thankfully the short charge emissions greatly predominate. But the lengthy emissions are also there, and from Figure III one can determine the percentage of them. The following performance characteristics were determined from the data. (See Table II).

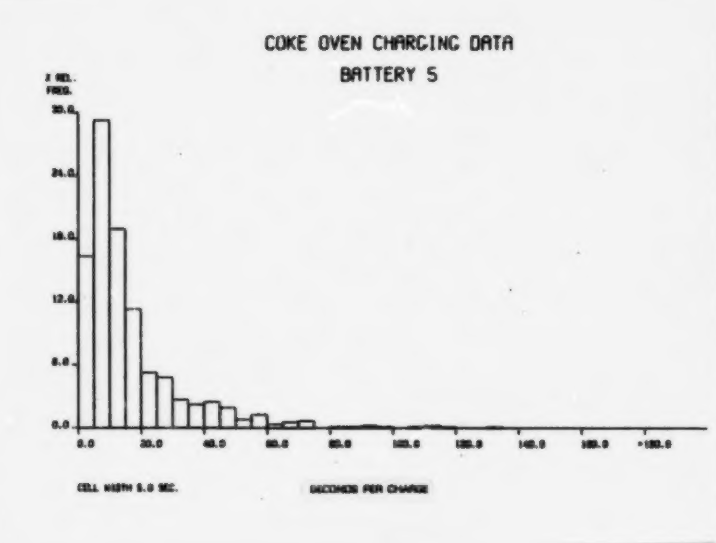
FIGURE 1

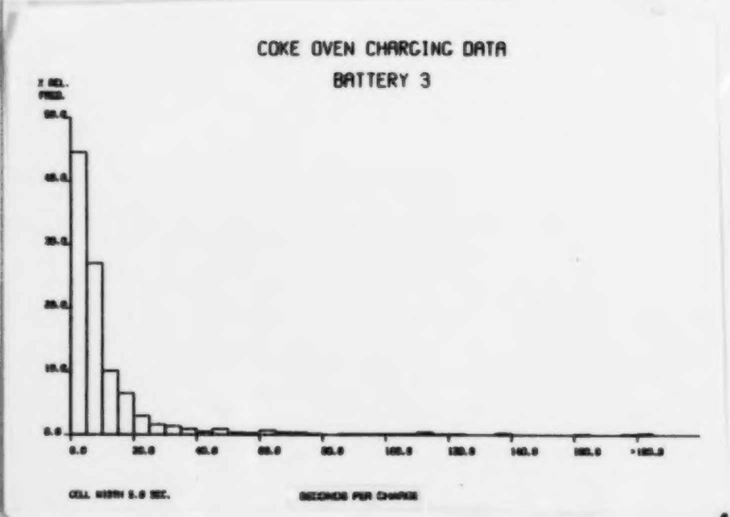
HISTOGRAMS OF INDIVIDUAL COKE OVEN CHARGE EMISSIONS


COKE OVEN CHARGING DATA
BATTERY 1


COKE OVEN CHARGING DATA
BATTERY 4


COKE OVEN CHARGING DATA
BATTERY 2


COKE OVEN CHARGING DATA
BATTERY 5


COKE OVEN CHARGING DATA
BATTERY 3

BATTERY 6

INDIVIDUAL CHARGE EMISSION

TIMES NOT AVAILABLE.

FIGURE 1

HISTOGRAMS OF INDIVIDUAL COKE OVEN CHARGE EMISSIONS

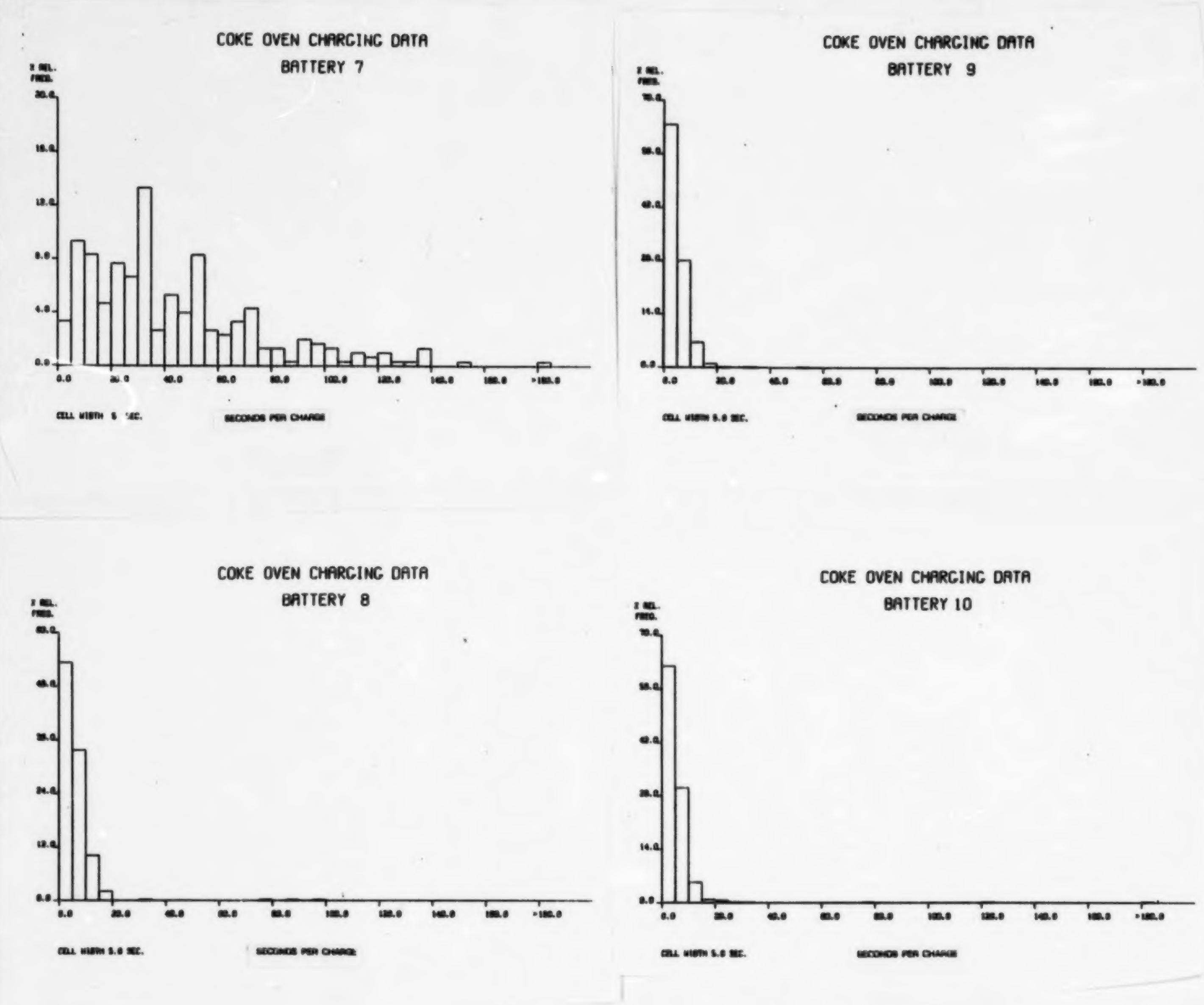


FIGURE II

HISTOGRAMS OF AVERAGE COKE OVEN CHARGE EMISSIONS

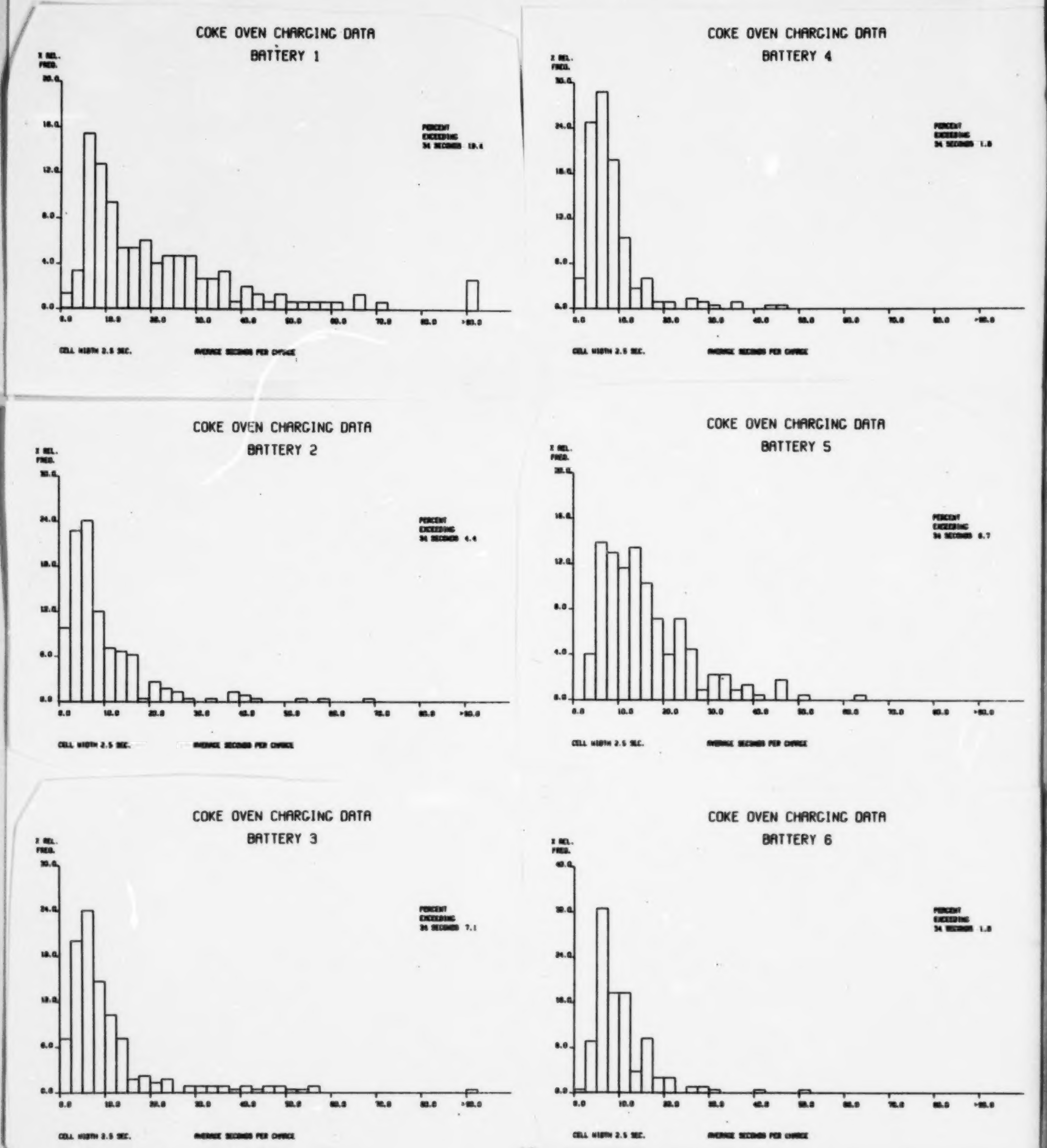


FIGURE 11

HISTOGRAMS OF AVERAGE COKE OVEN CHARGE EMISSIONS

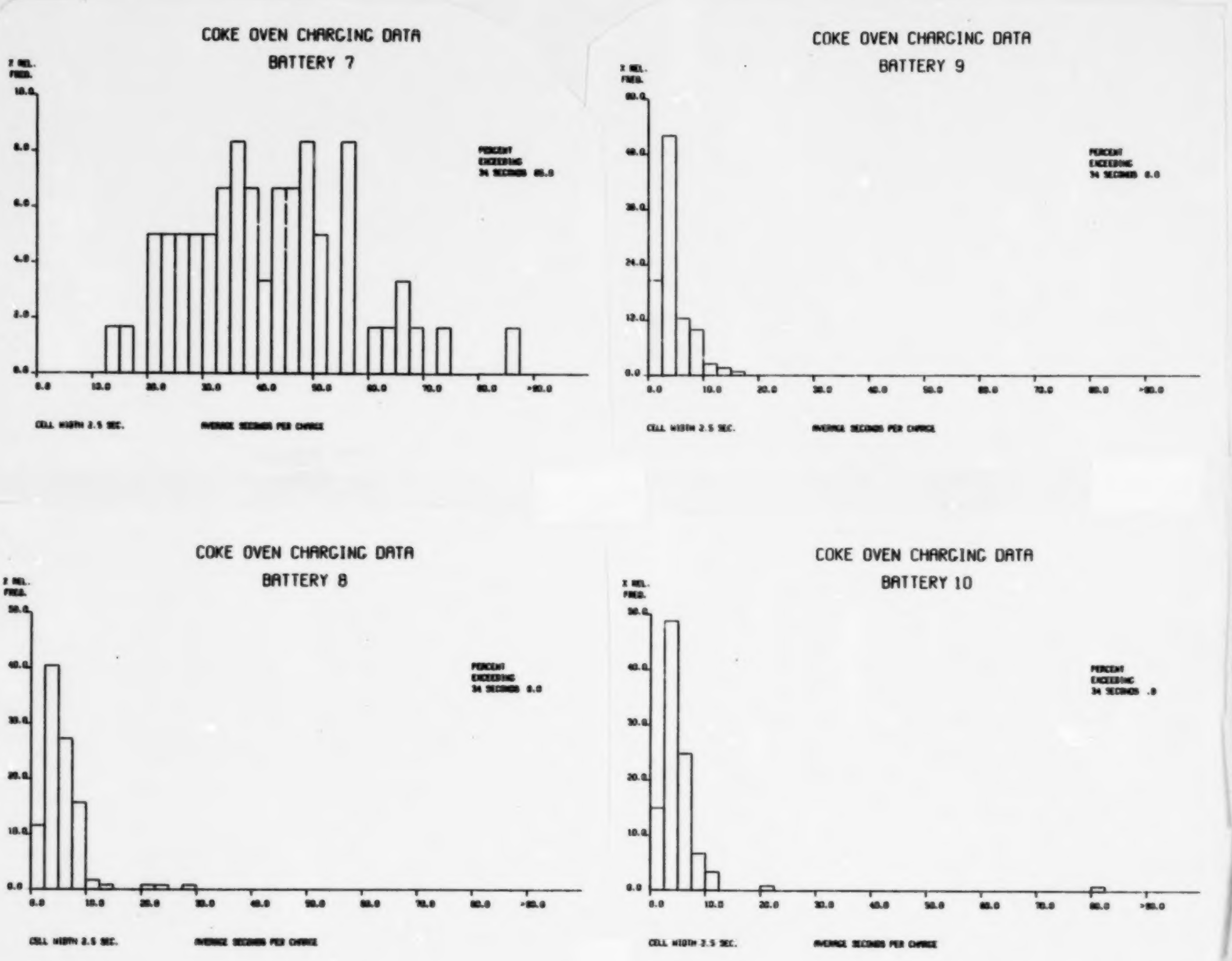


FIGURE III

CUMULATIVE FREQUENCY - PER CENT OF CHARGE EMISSIONS SHORTER THAN OBSERVED TIME

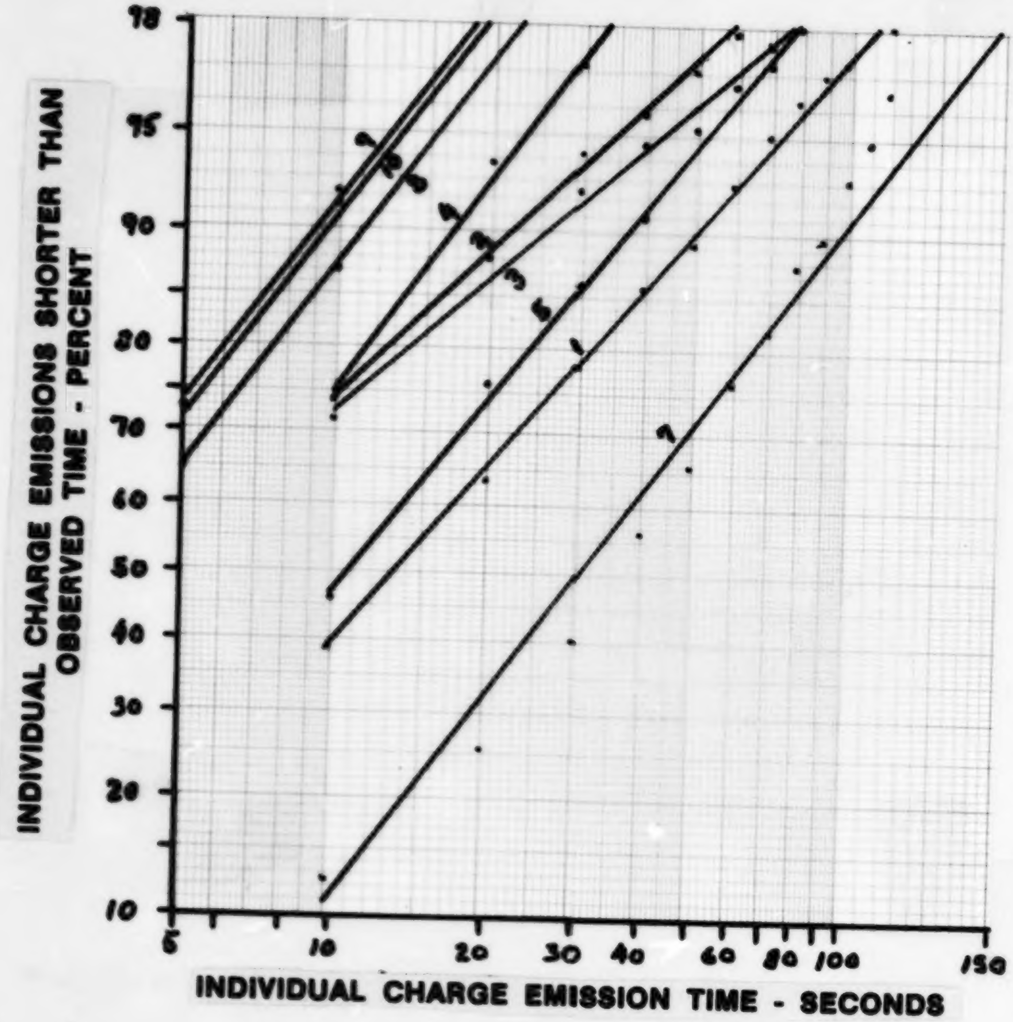


Table II - Average Emission Time Characteristics

	Collecting Mains	Average Charge-Sec.	% Exceeding 25 Sec.	% Exceeding 34 Sec.
Battery 1	1	23.5	31.6	19.4
Battery 2	1	9.7	6.2	4.4
Battery 3	1	11.2	9.3	7.1
Battery 4	2	8.3	3.6	1.8
Battery 5	1	16.0	14.3	6.7
Battery 6	2	10.0	3.2	1.0
Battery 7	1	42.5	83.3	65.0
Battery 8	2	5.7	0.8	0.6
Battery 9	2	4.2	0.4	0.4
Battery 10	2	5.2	0.8	0.6

E. Discussion of Charge Time Distributions

For a coke battery to meet a standard of 125 seconds visible charging emission per five consecutive charges, it would have to average less than 25 seconds per charge, and similarly to meet a standard of 170 seconds per five charges, which is the standard in two important coke industry states, it would have to average less than 34 seconds per charge. In Figure I and Table II it is apparent that all the batteries in this survey, except Battery 7, average well under 25 seconds per charge. However, in Figure I it is apparent that every battery also produced some long emissions. In Figure II the emission times were cumulated for 4, 5 or 7 charges, whichever was required by the local regulation. Then the cumulated time was divided by the number of charges to get the average charge emission length. This figure shows that on all batteries except 8 and 9 a not inconsiderable number of inspections would have been failed. For example, exemplary battery 6 exceeded 25 seconds average emission time in 3.2% of the observations and 34 seconds in 1.0% of the observations. Even batteries 8 and 9 had a rare long emission that would have caused failure of the inspection. None of these well controlled batteries would always have passed a compliance inspection.

Although none of the batteries in this survey is brand new, several employ all the equipment that is presently believed to be LAER technology. The data suggest any battery using this technology will probably not be able to consistently achieve the LAER standard of 55 seconds per five successive charges visible emission.

F. Effect of Battery Physical Features on Charge Emissions

In this survey the best performance is achieved by Batteries 6, 8, 9 and 10 which are short batteries with double collector mains. The 6 meter battery (No. 4), which also has double collector mains, performs almost as well as the short batteries with double collector mains. Batteries 1, 2, 3, 5 and 7 which have single collector mains, perform well on the average, but are not as consistent as the double main batteries. They have more long charge emissions than the double main batteries have.

III. The Coke Battery Operator's Problem With Chance

A. The Equipment Problem

If everything is working well, the steam aspiration is strong, the "tunnel head" space above the coal is open, and inleakage through oven openings is controlled, then the charging emissions will be brief or even entirely captured within the oven. However, a typical battery has thousands of parts that have some effect on charging emission time. All of these parts must function well for every charging emission to be captured and held within the oven.

B. The Personnel Problem

In addition to the equipment having to work right, the performance depends on people, to operate the equipment in the right sequence, to carry out every step correctly, and, to maintain the equipment diligently.

Automation can eliminate some human errors, but automatic equipment is very vulnerable to the severe heat, cold and moisture plus the pounding it will receive at the coke battery. Therefore, machinery that is too automatic seldom works. The optimum amount of automation on a coke battery is far less than it would be in a more temperate location. The optimum automation for a coke battery still relies heavily on human operators.

C. The Long Emission Time

There are some types of equipment malfunctions which should be apparent (but not necessarily correctable immediately) before a charge begins, but others are not. For example, a misaligned drop sleeve should be apparent. But, a shorted electrical wire might not be noticed before there is a loss of electrical function that has already resulted in a long charge emission. There are also "malfunctions" caused by changes of the flow properties of the coal. Sometimes coal moisture or other characteristics can change the coal flow behavior enough to result in a long emission time. Freezing weather can prevent the coal from flowing freely as needed for good stage charging. These coal flow problems are likely to cause a string of long charge emissions.

D. Operators Viewpoint

Taking all of these factors together, unpredictable equipment malfunctions, unpredicatable human errors, and variable coal properties, the operator usually doesn't know in advance when a long charge emission is coming. But, he knows by the law of averages that some long charge emissions are going to come. Consequently, when an Agency Persons says you may not exceed 125 seconds for five charges, the operator feels it is an inequity. It is like demanding that a baseball player bat .300 in every ball game. A good player can bat .300 for a season, but he knows he can't do it in every game. Similarly, a good coke battery operator can average less than 125 seconds for five charges but he will go over 25 seconds on a significant fraction of the charges. Occasionally just one charge will exceed 125 seconds.

IV. Emission Quantity Versus Allowable Emission Time

A. Operators Want Zero Emissions

An agency engineer testified in a public hearing that shortening the emission limit from 170 seconds per five charges to 125 seconds per five charges would reduce coke oven charging emissions by 45/170ths or 26%. This would be true only if the emission on each charge occurred for the full time allowed by the standard. This in turn implies a degree of control over charging emissions which does not exist in practice. In reality the operators think this way: "A bad charge can happen at any time, and when it occurs it is likely to use up our whole allowable emission time. Therefore, we had better make each charge emission as close to zero as we can."

Figure II corroborates this. These batteries are required in one case to average under 34 seconds, some to average under 19 seconds, and one to average under 11 seconds. All but one do much better than required. These batteries are not just barely meeting their allowable emission.

B. Comparison of 170 Seconds to 125 Seconds Standard

Operators I have questioned felt that for all practical purposes a standard of 170 seconds holds emissions down as well as a standard of 125 seconds per five charges. They must use the same equipment, work practices, and training to attempt to meet either standard. As discussed in the preceding paragraph, there won't be any difference in the average charge emission time. The only difference is that the battery will violate the 170 second standard somewhat less frequently.

X. Recommending a More Equitable Kind of Charging Emission Standard

A. The Batting Average Measures Ability in Baseball

Returning to the baseball analogy, baseball fans recognize that the all around best measure of a player's batting ability is his medium to long term batting average. They realize that hitting a baseball under game conditions is a statistically variable function. Even though the player yearns to hit, he cannot do it every time or even once in every game. A single game batting average is not a reliable measure of batting ability. A manager who punished players for failure to hit in each game would be thought capricious and would probably provoke a confrontation with the players union.

Similarly, there is no way humanly possible to eliminate long charge emissions from a coke battery. Although the operators know that with good equipment, good maintenance and careful attention to work practices they can increase their chances to pass inspection against a limit of 125 seconds for five charges, still in their perception it is inevitable that there will be violations. If they are to be cited for violations, they perceive this to be inequitable and they find themselves in a disagreeable position.

B. A Batting Average for Coke Oven Charging Emissions

I suggest that a different kind of charging emission standard is needed. It should be more in the nature of a medium to long term batting average and not have the nature of a single game batting average. A good coke battery operation will have the great majority of its charging emission time short. But even the best operated batteries also will have unpredictable occurrences of long charging time. The coke battery has to be allowed occasional bad charges, and even a string of bad charges. My suggestion is purely a personal one. This is not an industry opinion nor a Republic Steel opinion. My suggestion is that the charging emission time for single charges ought not to exceed 25 seconds more than X% of the time. The data suggest X could be larger for single main batteries than for double main batteries, and larger for tall batteries than for short ones. In general, X should take into account design features, condition, age and remaining life of the battery. The very select batteries studied in this paper (with one exception) had X in the range of 5 to 35. One must bear in mind that whereas Table II deals with average emissions, the X I am suggesting would be derived from individual emissions and might be larger than the values in Table II. For example, on battery 5, while 14.3% of the daily averages exceed 25 seconds, 17.2% of the individual charge emissions exceed 25 seconds. Additionally, X should be adjusted upward or downward according to the number of observations in the sample. It should be larger for 50 observations than for 500 observations.

I believe the "batting average" for determining compliance should be based on at least a month of data (preferably a quarter) where five consecutive charges are timed daily, five days a week. This, of course, would require the company observers to inspect themselves because no agency can afford the manpower to inspect so frequently. But, I believe the experience already obtained in several states with self-reported coke battery observations shows the majority of company observers to be trustworthy. I believe the agencies will easily discover which batteries can seldom pass inspection when agency personnel are present to observe.

C. All Around Ability Versus Batting Average

As important as hitting is to baseball, there are other abilities that a player needs. Since no player is equally as strong at all facets of the game, a manager may be willing to forego a certain amount of hitting ability to get outstanding fielding or base running. Though I have not studied door leaks and topside emissions as thoroughly as I have studied charging emissions, I have data (not presented in this paper) that indicates exemplary charging emission control seldom combines with exemplary door leak control and topside leak control on the same coke battery. There may be interactions between one and another. Agency people may have to adapt a pragmatism toward balancing the various facets of coke battery emissions control.

VI. Conclusion

This paper discusses the problem of establishing an equitable and effective coke oven charging emission standard. The solution depends on having a model that describes accurately the behavior of coke oven charging emissions.

Data collected by the author from ten of the best controlled coke oven batteries in the industry, two of which are considered exemplary batteries by U.S. EPA reckoning, are skewed distributions. These data imply that even the best controlled batteries will have some charges with long emission times. Nevertheless, the average charge emission time is short.

The inappropriateness of present standards of the type which limit visible emissions to L seconds per N charges is discussed. This paper suggests that an equitable emission standard ought to permit occasional long charge emissions. It is recommended that the standard measure performance over a month or more of inspections and require that no more than X% of the individual oven charges exceed 25 seconds emission time. For the very select batteries studied in the paper, X could be in the range of 5 to 35 depending on the features of individual batteries including the number of collection mains, and whether the battery is short or tall. Also for statistical reasons X should be adjusted to accord with the number of observations in the sample.

The SCAT System for Fugitive Particle Emission Control

by
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Air Pollution Technology, Inc.
and
Dennis Drehmel
U.S.-E.P.A

ABSTRACT

The Spray, Charging and Trapping (SCAT) scrubber system is unique fugitive emission control system being developed by Air Pollution Technology, Inc. It has many potential applications in the Iron and Steel industry including major sources such as coke ovens and blast furnaces. The SCAT uses air curtains and push jets to contain, divert and convey the fugitive emissions into a charged spray scrubber.

Experiments were performed on an 8,000 CFM bench-scale spray scrubber to verify the theory and demonstrate the feasibility of collecting fugitive particles with charged sprays. The effects of charge levels, nozzle type, drop size, gas velocity, and liquid-to-gas ratio were determined experimentally. The experimental data and theoretical predictions are presented in this paper.

A prototype SCAT system was built and tested on a crosswind and on a hot, buoyant smoke plume. Theoretical predictions and experimental data are presented.

INTRODUCTION

Controlled disposal is the permanent way to control fugitive particle emissions because it prevents the redispersal of particles. This technique involves gathering and conveying the fugitive emissions to particulate control devices. Present methods used to contain fugitive emissions, such as total building enclosure and evacuation, or secondary hooding at the local source of emissions, are ineffective and costly.

The SCAT (Spray, Charging, and Trapping) scrubber system is a novel, controlled disposal scrubber system for controlling industrial process fugitive emissions. It uses air curtains and/or air push jets to contain, divert, and convey fugitive particles into a fine particle scrubber. The SCAT scrubber uses charged water sprays for removing particles entrained in the gas stream.

A schematic drawing of the SCAT system is shown in Figure 1. The SCAT system uses four major components: (1) air curtain or air push jets, (2) particle charger and charged water sprays, (3) entrainment separator, and (4) water treatment and recycling system. There is no one fixed design or configuration for the SCAT and it is not necessary for a SCAT to have all four components. Its design varies from source to source.

The most important features and advantages of the SCAT system are listed below.

1. Inexpensive, simple design.
2. Portable, does not interfere with process equipment.
3. Minimum use of solid boundaries enabling access to the source.
4. Minimum use of ducting and hooding.
5. Deflects crosswinds.
6. Contains hot buoyant plumes.
7. Enables controlled disposal of particles.
8. Flexible design to suit individual process.
9. Energy efficient fine particle collection.

The purpose of this work was to evaluate available engineering design models for the SCAT system. Specifically this included evaluating air curtains and charged spray models. Although air curtains and charged sprays have been

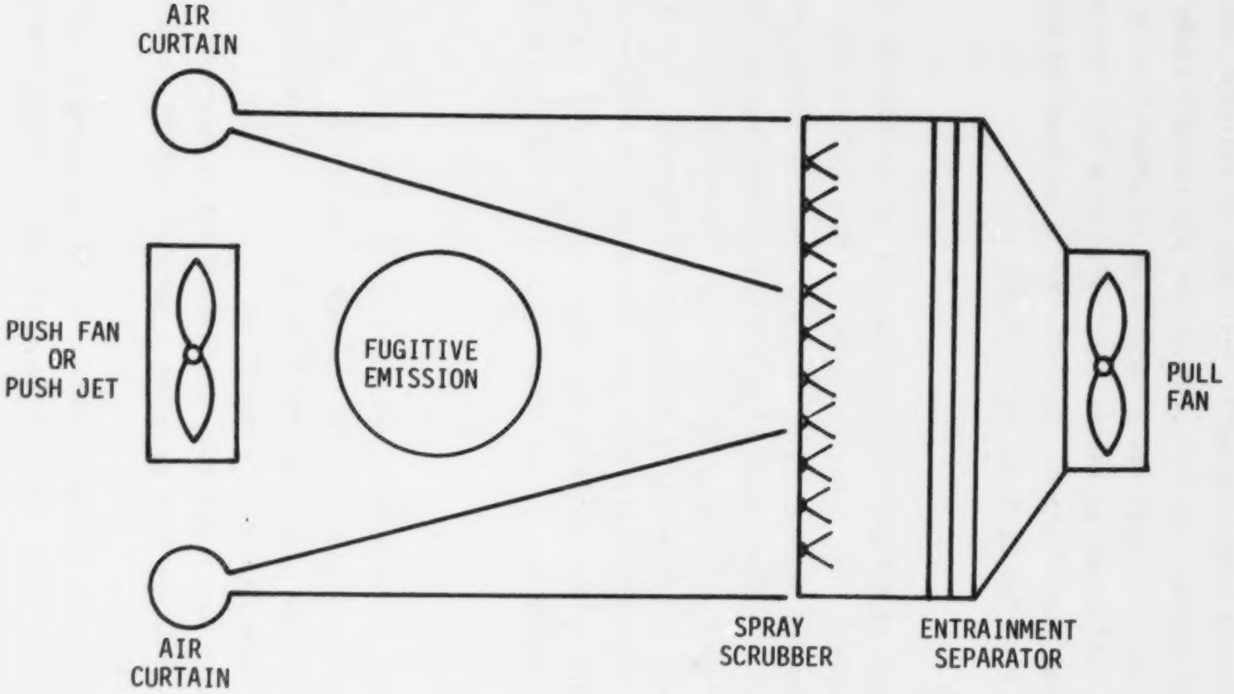

Figure 1. Example of SCAT system arrangement.

studied and used in industry for years, there are surprisingly few useful design models and few studies reporting sufficient data to evaluate these models.

This work was broken into two phases: the air curtain study and the charged spray study. The goal was to arrive at an understanding of the SCAT system which was sufficient to enable the design of a SCAT system for any specific industrial installation. Details of the engineering models and calculations are reported by Yung, et al (1980).

AIR CURTAIN STUDY

An air curtain is a sheet of air blown out of circular or rectangular nozzles at high speed. Air curtain design for the SCAT system requires information on several parameters of the jet stream including the velocity distribution, jet expansion angle, the air entrainment ratio, and the effects of hot buoyant plumes and crosswinds. The jet expansion angle determines the overall cross-sectional dimensions of the receiving hood. The air entrainment ratio determines the volumetric flowrate of the gas to be cleaned. The crosswind and/or buoyant plumes dictate the placement of air curtains and the receiving hood. Design models for these parameters were evaluated experimentally in this study.

Air Curtain Manifold

The air curtain distribution manifold should give a uniform discharge velocity distribution along the manifold length to perform properly. In addition, the discharge direction should be as close to perpendicular to the flow direction in the manifold as possible.

To obtain a uniform discharge, a constant static pressure must be maintained along the duct. This was done by using a tapered duct to counterbalance static regain in the manifold.

The discharge angle was maintained near 90° by using a continuous slot nozzle divided by deflector vanes which protruded 9 inches from the air curtain duct. This is illustrated in Figure 2.

Jet Expansion Angle and Air Entrainment Ratio

The jet expansion angle and air entrainment ratio were determined experimentally. They were calculated from velocity distribution measurements at several downstream locations from the manifold. The calculated jet expansion

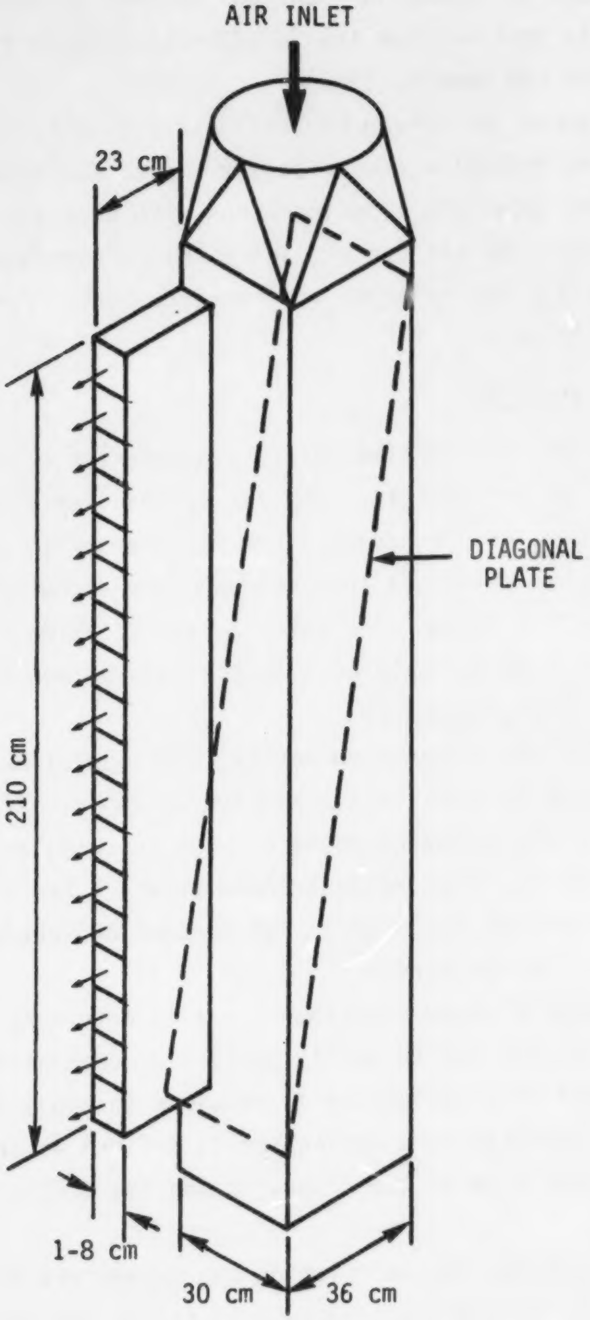

Figure 2. Air curtain distribution duct.

angle was about 25° which is identical to that predicted for a pure momentum jet, but it is smaller than the 30°-40° reported in the literature (Tuve and Priester, 1944 and Hemeon, 1963).

The measured jet stream centerline axial velocity decay agrees with that predicted from Prandtl's eddy viscosity model for turbulent flow as shown in Figure 3. The total air flow increases with distance from the air curtain manifold because the air curtain jet entrains surrounding air. The air entrainment ratio was measured and the data agree fairly well with predictions as shown in Figure 4.

Crosswind Experiments

Experiments were carried out to evaluate the effect of crosswinds on the trajectory of an air curtain. The air curtain jet may be used either to deflect the crosswind so that it bypasses the scrubber or to entrain and deflect the wind and fugitive emissions into the scrubber downwind from the emission source. In either case the design of a specific installation will require the ability to predict the momentum balance between the wind and air curtain and thus the resultant air flow trajectory.

Wind deflection depends on several SCAT operating parameters such as the distance between the air curtain and the scrubber, air curtain slot width, slot exit velocity, the incidence angle between the wind and air curtain jet stream, and the wind speed. The incident angle at which the air curtain meets the wind is the most important parameter. For maximum deflection, the jet stream should be at 45° opposing the wind.

The purpose of these experiments was to determine the requirements for deflecting crosswind and to verify published correlations. For the SCAT system, complete wind deflection is required to avoid disturbances in dust containment. Complete wind deflection is defined as the condition for which the resultant air flow of the crosswind and the SCAT air curtain bypassed the SCAT scrubber.

Several formulae for correlating the parameters mentioned above are available in the literature. Instead of fixing the incident angle at 135°, which gives the maximum range, wind deflection experiments were performed by fixing the range (distance from air curtain to scrubber), wind speed, air curtain slot width, and slot exit velocity and varying the incident angle for

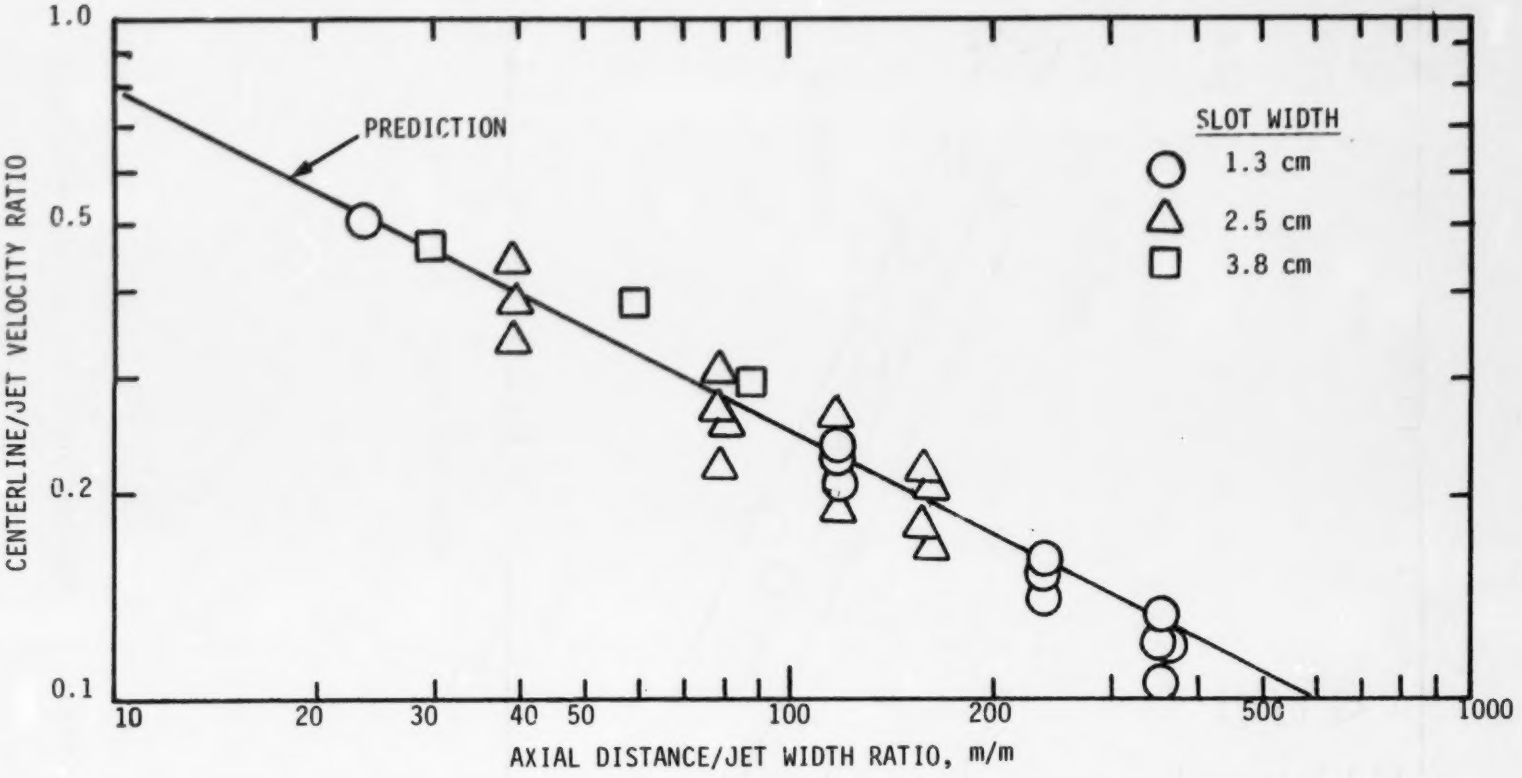

Figure 3. Measured and predicted centerline velocity decay.

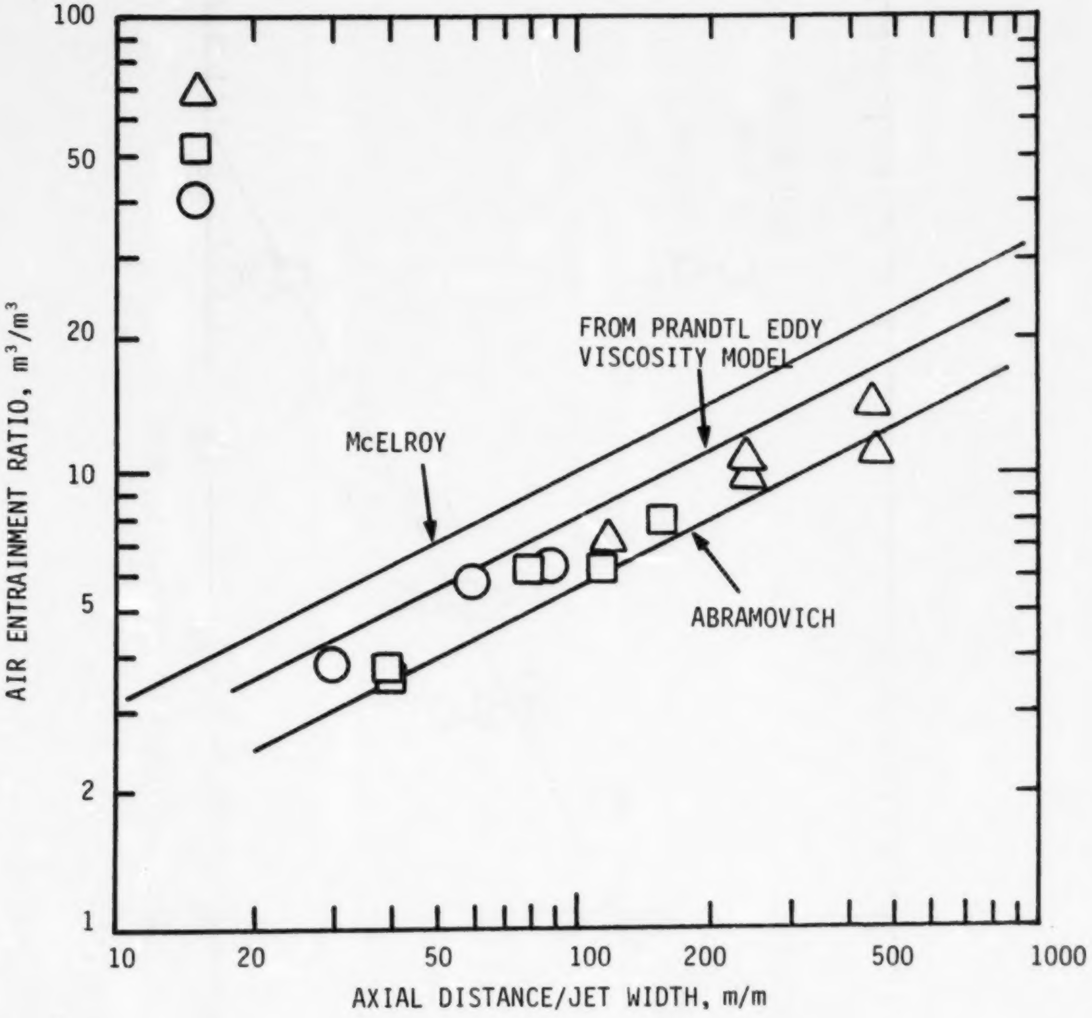

Figure 4. Measured and predicted air entrainment ratio.

wind deflection. The measured angle was then compared with predictions. It was found, as shown in Figure 5, that the measured angle agrees with that calculated from theory (for details on the theory see Abramovich, 1963). Thus the deflection of a crosswind can be accurately predicted from the air curtain design and operating parameters.

Hot Source Experiments

In many metallurgical processes very hot fugitive plumes containing high concentrations of particles are released. The most efficient and economical way to clean these plumes would be to capture them at the source where the concentration is highest and gas volume lowest. However, for practical reasons such as the presence of overhead cranes, it is impossible in many cases to capture the plume at the source or even vertically above the source with fume hoods. In these situations a SCAT system could be applied to control the emissions. An air curtain could be used as the ceiling to contain the fumes and dust and horizontally displace the plume into a receiving hood or directly into a scrubber if space is available for its installation.

Experiments were done to study the feasibility of containing hot plumes with air curtains. The hot source was simulated with an open top furnace which had a natural gas, open flame burner. The furnace was a rectangular box lined with insulating fire-bricks. There was an opening on top of the furnace for the hot gas to exit.

The furnace was located at the center of the SCAT system. The distance between the air curtain assembly and the spray scrubber was 3.1 m. Since the operation of the burner was fixed, the "ceiling" air curtain location was adjustable so that the jet stream could meet the hot plume at different temperatures. At a height of 60 cm above the furnace, the hot plume had a temperature of 500°C and a velocity of 2 m/s.

The effect of buoyancy on the air curtain flow field was deduced by comparing the velocity and temperature profiles before and after the burner was turned on. Fly ash particles were also injected into the furnace with the ceiling air curtain off and on for hot plume trajectory observations.

A correlation for predicting the hot plume trajectory was derived. It is based on a momentum balance which accounts for the buoyancy and momentum of the plume. Figure 6 shows the experimental layout and predicted and observed

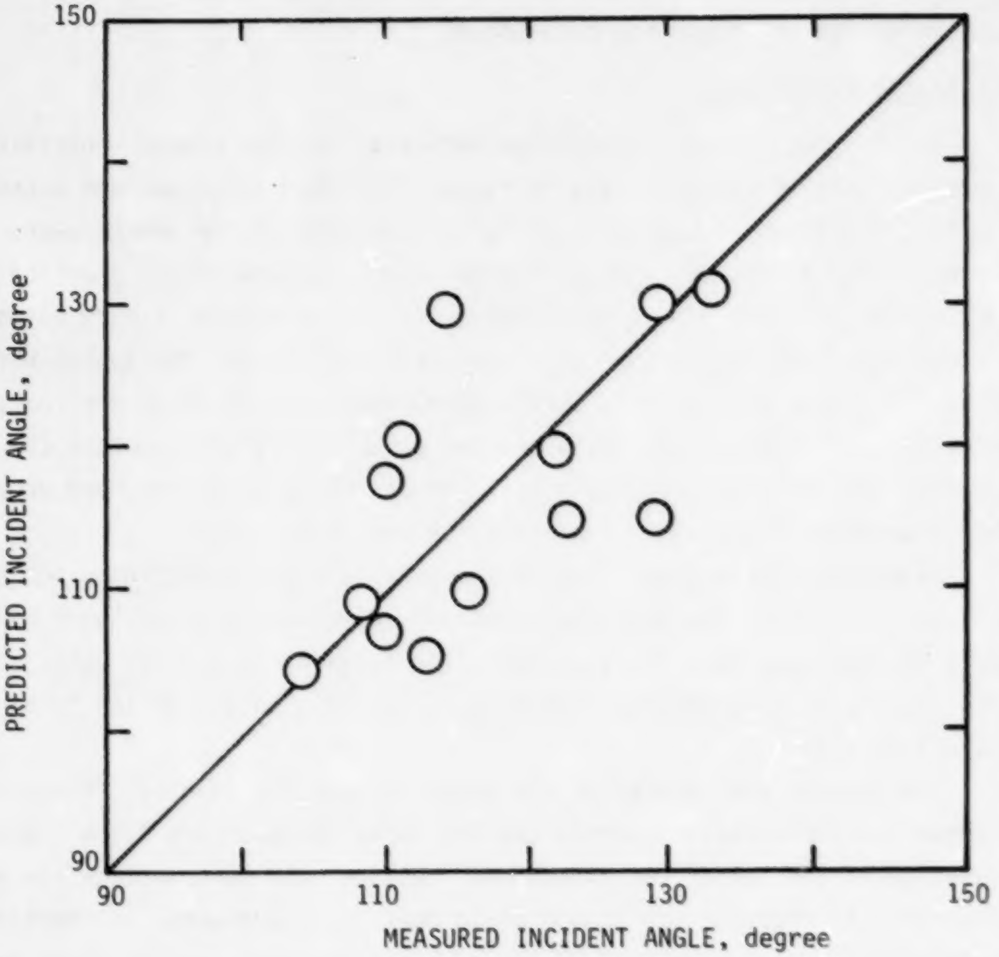

Figure 5. Measured and predicted incident angles for wind deflection with an air curtain.

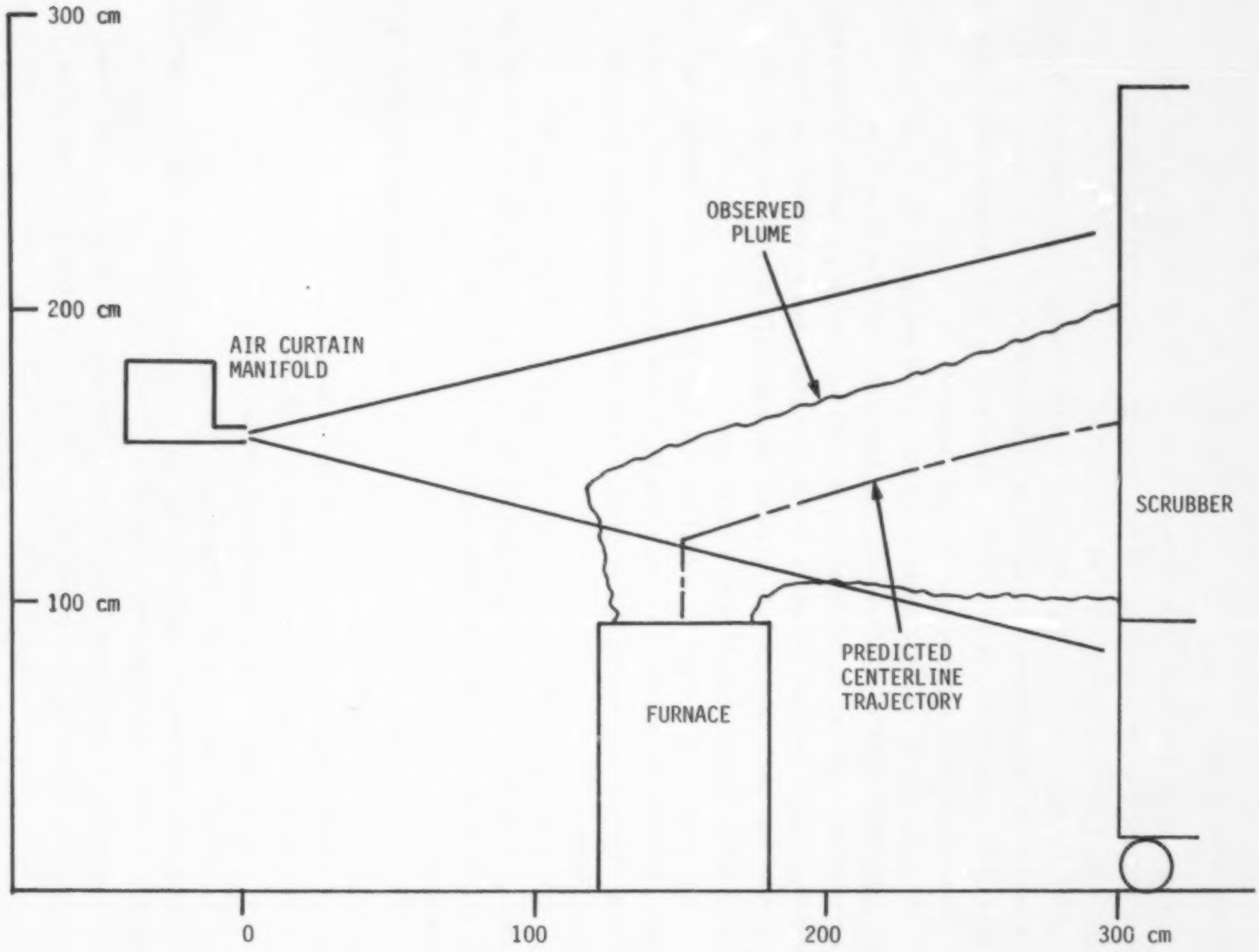

Figure 6. Hot plume trajectory and flow pattern.

plume center line at the scrubber inlet. Predicted plume rise is slightly higher than observed.

CHARGED SPRAY STUDY

For a spray scrubber collection by drops is the principal collection mechanism and the particle penetration for a given size particle may be calculated from theory (Calvert, et al, 1975).

The charged spray scrubber has been studied theoretically and experimentally by a number of researchers, including Melcher and Sacher (1974), Lear, et al, (1975, 1976), and Pilat, et al, (1975, 1976, 1978 a, b). However, data reported by these researchers were not sufficient to verify the theory.

An experimental charged spray scrubber system was built to obtain design data under well defined conditions. The scrubber consisted of a flow straightening section, an inlet particle sampling section, a particle charging section, a spray section, an entrainment separator, and an outlet sampling section. The spray section consisted of two removable spray banks and their configuration varied depending on nozzle type.

The drops were charged by induction. A high voltage grid assembly was placed in front of nozzles to induce charge on the water drops. The distance between the grid and nozzle was adjustable to allow for maximizing the drop charge level.

Two types of nozzles were tested. The hook type nozzle (type "A") produced drops with mean diameter around 240 µm at a nozzle pressure of 430 kPa. The discharge coefficient and spray angle for this nozzle were 0.63 and 100°, respectively.

The particle collection efficiency of the spray scrubber was measured for the following four conditions:

1. ND/UP (Neutral drops/uncharged particles),
2. CD/UP (Charged drops/uncharged particles),
3. ND/CP (Neutral drops/charged particles), and
4. CD/CP (Charged drops/charged particles).

Note that the "uncharged" particles may not be neutral because they may carry some charge when they enter the scrubber.

Figures 7, 8 and 9 show typical data along with theoretical predictions. The particle collection efficiency of the scrubber was found to improve by

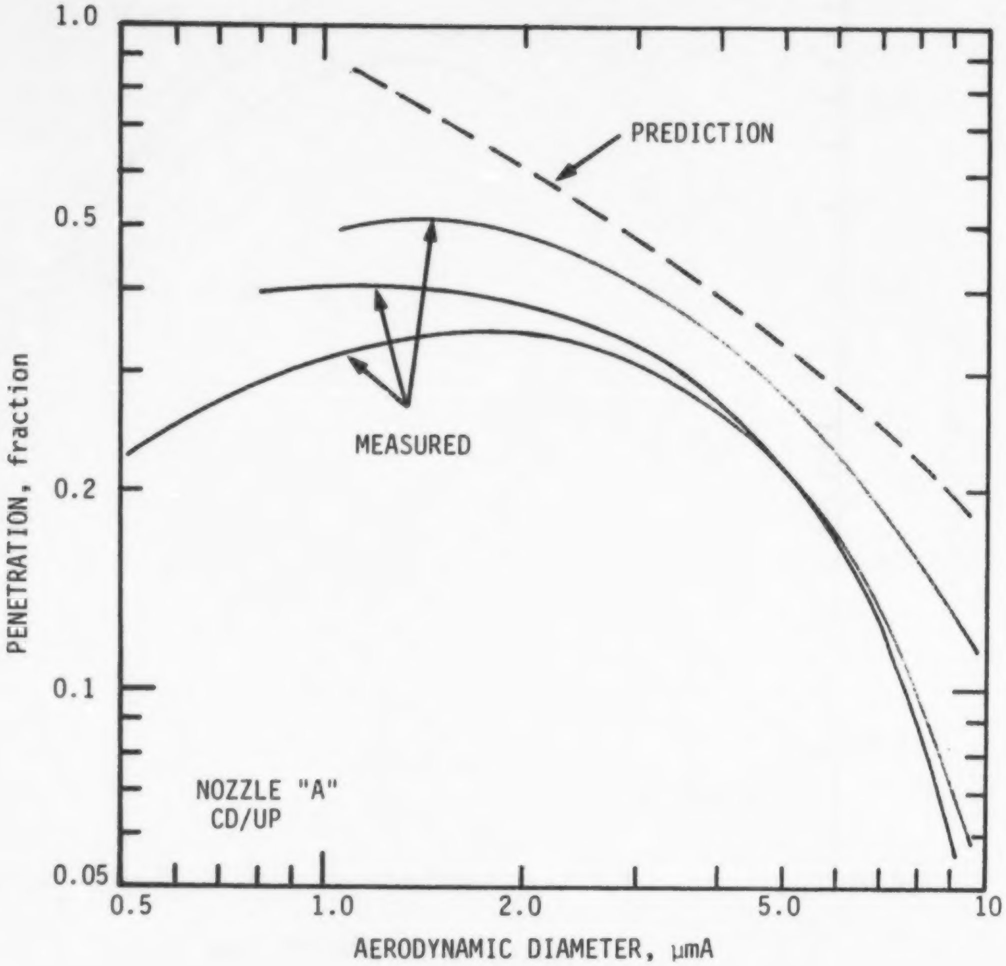

Figure 7. Charged spray performance for image charge with nozzle A.

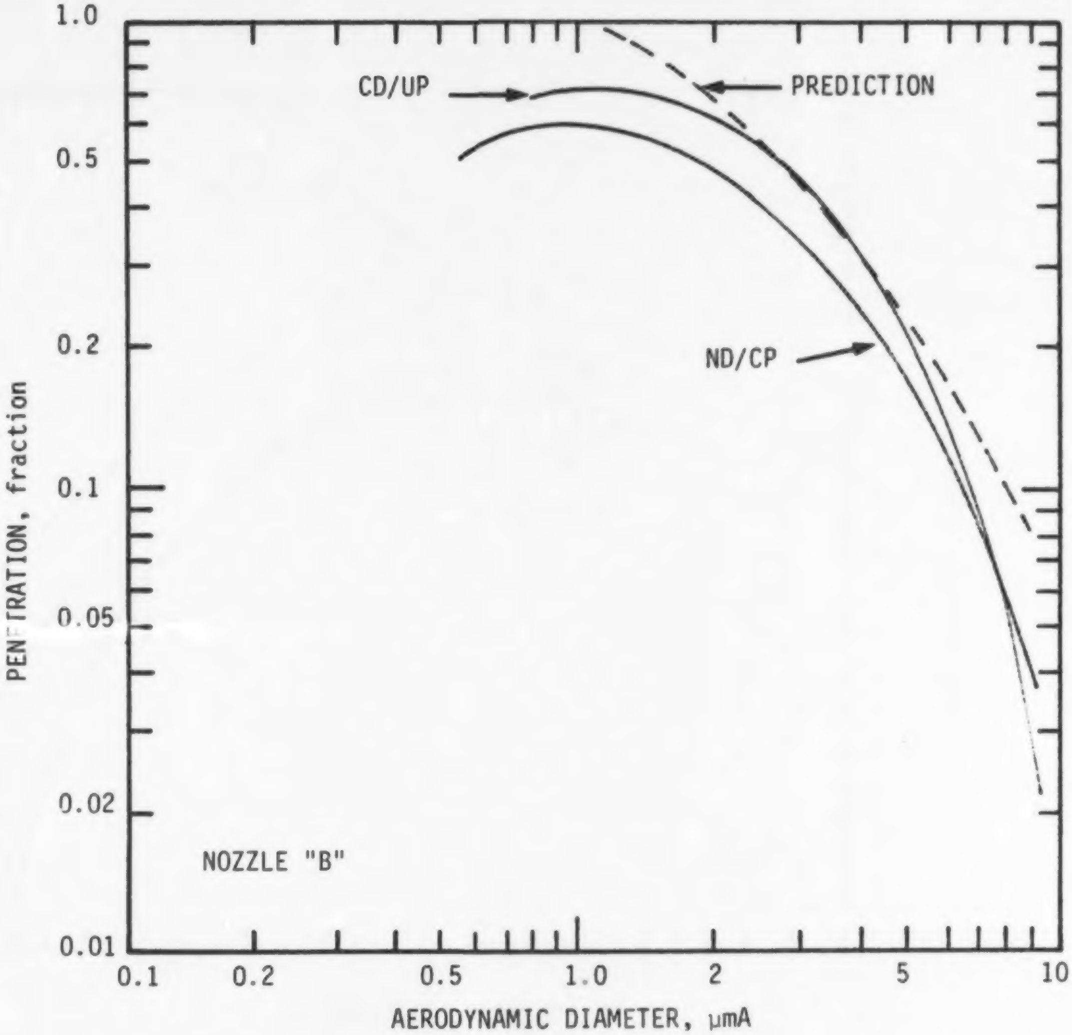

Figure 8. Charged spray performance for image charge with nozzle B.

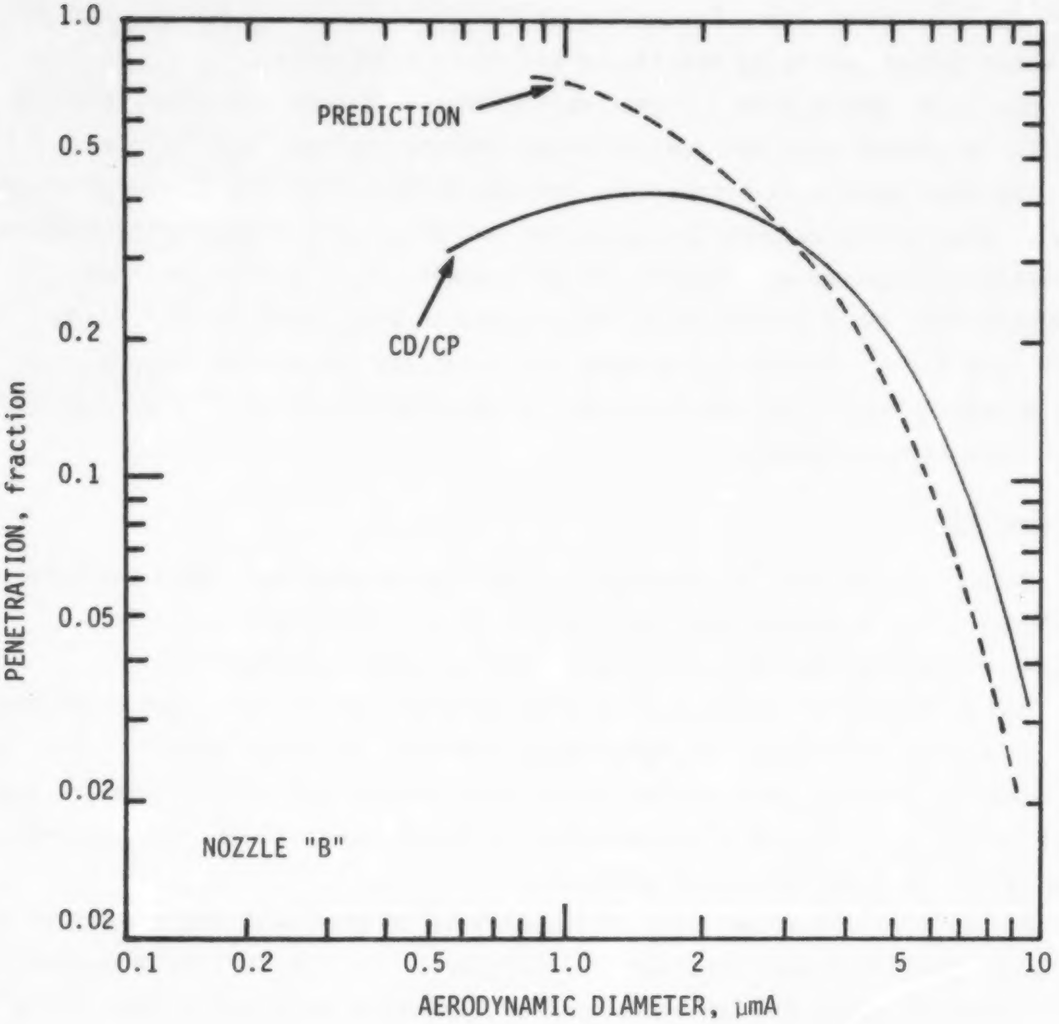

Figure 9. Charged spray performance for coulombic force with nozzle B.

charging either the water drops or the particles. Measured drop charge and particle charge levels were +5.8 x 10^{-7} C/g and -1.5 x 10^{-5} C/g, respectively. Test particles were hydrated lime with mass median diameter of 3.5 μmA and geometric standard deviation around 2. Further improvement was obtained when the drops and particles were oppositely charged. The improvement was more with submicron particles. For particles larger than 5 μmA diameter, charging the water and/or particles has little effect on efficiency.

Hook type nozzle gave a higher collection efficiency than the pigtail type. This is consistent with the smaller drops produced by hook type nozzles.

The data agree with predictions for the ND/UP conditions (spray scrubber only). When either or both the particles and drops were charged, the measured collection efficiency was higher than that predicted. In fact the theory predicted that there should be no improvement in efficiency for ND/CP and CD/UP conditions. Slight improvement was predicted for the CD/CP condition. Therefore a better theoretical design model is required for predicting performance of charged spray scrubbers.

CONCLUSIONS

A simple technique for controlling fugitive process emissions has been developed. The technique involves the use of air curtains and air jets to contain and convey the emissions into a nearby spray scrubber.

The collection efficiency of a spray scrubber was investigated experimentally. The collection efficiency was improved by charging the water and/or the particles. The measured particle penetration agrees with theoretical predictions for the ND/UP condition. For the electrostatically augmented scrubber, the measured penetration is lower than that predicted.

Air curtains have been used in industry to contain dust but no carefully performed study has been reported in literature. The air curtain developed in the present study can achieve a smaller expansion angle and a lower entrainment ratio than those reported in the literature. Small expansion angles and entrainment ratios are beneficial to the control of fugitive process emissions with the SCAT system.

The effects of crosswind and the containment of a hot buoyant plume were also studied. It has been shown that available theory (Abramovich) gave reasonable predictions for the air curtain range, trajectory of the air curtain axis in the presence of a crosswind, and the required spray scrubber rotation angle for intercepting the jet stream. Therefore, in operating the SCAT system under crosswind conditions, there is a rational basis for locating the air curtain and spray scrubber relative to the crosswind and emission source.

The air curtain was successful in containing a hot buoyant plume. At an air curtain/spray scrubber separation of 3 m, an air curtain with slot width of 5.1 cm and air exit velocity of 20 m/s can contain a hot plume which is rising at a velocity of 200 cm/s and has a temperature of 470°C. The trajectory of the plume can be predicted from a plume rise formula.

We have done most of the necessary basic research in the present study. The general SCAT system can be applied to many kinds of sources. The next step is to select a source and demonstrate the feasibility of the SCAT system.

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FUGITIVE EMISSION CONTROL OF OPEN DUST SOURCES

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ABSTRACT

This paper presents empirically developed predictive emission factor equations for open dust sources in iron and steel plants. The ranges of applicability and the precisions of the equation are discussed. Presently, the equations for the two open dust sources of greatest magnitude (unpaved and paved roads) have good precision, with 68% of the predicted values lying within factors of 1.21 and 1.53 of the measured values for unpaved and paved roads, respectively.

Also presented are the results of tests performed on control techniques to mitigate fugitive dust from vehicles traveling on unpaved roads. Limited testing of chemical dust suppressants for industrial unpaved roads indicates a high initial control efficiency (exceeding 90%) which decreases more than 10 percentage points within about 24 hr after application. The emission factor equations are shown to be useful in estimating control efficiencies in the absence of adequate efficiency test data.

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FUGITIVE EMISSION CONTROL OF OPEN DUST SOURCES

INTRODUCTION

Two types of fugitive emissions occur in the iron and steel industry--process fugitive emissions and open dust source fugitive emissions. Process fugitive emissions include uncaptured particulates and gases that are generated by steel-making furnaces, sinter machines, and metal forming and finishing equipment, and that are discharged to the atmosphere through building ventilation systems. Open dust sources are those that entail the generation of fugitive particulate emissions by the forces of wind and machinery acting on exposed raw, intermediate and waste aggregate materials during storage, transfer and disposal.

The ranking of the emissions potential of open dust sources at a given iron and steel plant or across the industry is an important tool in deciding where controls may be needed. This requires the development of emissions inventories, i.e., calculation of average emission rates for all significant sources at one or more plant sites.

Calculation of the emission rate for a given source requires data on source extent, uncontrolled emission factor and control efficiency. The mathematical expression for this calculation is as follows:

$$R = Me\,(1 - c)$$

where R = mass emission rate
M = source extent
e = uncontrolled emission factor, i.e., rate of uncontrolled emissions per unit of source extent
c = fractional efficiency of control

Because of the wide range of particle size associated with fugitive particulate emissions, it is important that the applicable particle size range be specified for the calculated emission rate. The particle size range should be that for which the uncontrolled emission factor and the fractional efficiency of control apply.

In a recent study of fugitive particulate emissions from integrated iron and steel plants, Midwest Research Institute[1] (MRI) determined that open dust sources (specifically, vehicular traffic on unpaved and paved roads and storage pile activities) ranked with fugitive emissions from steel-making furnaces and sinter machines as sources which emit the largest quantities of fine and suspended particulate matter, taking into account typically applied control measures. It became evident that open dust sources should occupy a prime position in control strategy development for fugitive particulate emissions within integrated iron and steel plants. Moreover, preliminary analysis of promising control options for both process sources of fugitive emissions and open dust sources indicated that control of open dust sources has a highly favorable cost-effectiveness ratio for particulate matter.

The industry-wide open dust source emissions inventory compiled by MRI utilized predictive emission factor equations developed by MRI based on field tests of a variety of uncontrolled sources at iron and steel plants. The most significant limitation to the reliability of the emissions inventory resulted from a lack of detailed knowledge of control efficiencies for various open dust source control techniques.

The following sections of this paper discuss: (a) the ranges of applicability and the precisions of the empirically developed predictive emission factor equations for uncontrolled open dust sources; and (b) the use of the emission factor equations to estimate the efficiencies of open dust source controls. In addition, the results of the tests performed on control techniques to mitigate fugitive dust from vehicles traveling on unpaved roads are presented.

A mixture of metric and English units was used in this paper. The symbol "T" refers to short ton, which is equivalent to 2,000 lb. The symbol "t" refers to the metric tonne, which is equivalent to 2,200 lb. An English-to-metric conversion table is presented at the end of this paper.

EMISSION FACTORS FOR UNCONTROLLED OPEN DUST SOURCES

The emission factor equations empirically developed by MRI[1,2] for uncontrolled open dust sources are shown in Table 1. The equations describe emissions of particles smaller than 30 µm in diameter based on a particle density of 2.5 g/cm^3. Although the equations represent anthropogenically uncontrolled emissions, most of the equations do incorporate natural control due to precipitation.

The precision of each equation in predicting measured emission factors over given ranges of independent variables has been calculated for those open dust sources which have been tested frequently enough to support a statistical analysis. Table 2 shows the one-sigma precision factors for the predictive equations. The one-sigma precision factor (f_1) is defined such that 68% of the predicted emission factors will be with a factor of f_1 of the measured values. The two-sigma precision factor (f_2) is defined such that 95% of the predicted emission factors will be within a factor of f_2 of the measured values.

The precision factors given in Table 2 are applicable only when the predictive equations are used with values of the independent variables that are within the ranges tested, which are also shown in Table 2. The equations are of undetermined precision when applied to sources for which independent variables lie outside of the ranges tested. Tables 3, 4, and 5 list the parameter ranges that have been measured by MRI[3] for road surface dust and aggregate materials within the iron and steel industry.

The precisions of the various equations differ extensively. The one-sigma precision factor for unpaved roads is 1.21, while the two-sigma precision factor is 1.46 based on 23 tests. Because unpaved roads are often the largest open dust source in an iron and steel plant, more effort has been placed on the testing of this source in relation to the others, with

TABLE 1 OPEN DUST SOURCE EMISSION FACTOR EQUATIONS

Source category	Measure of extent	Emission factor[a] (lb/unit of source extent)	Correction parameters
1. Unpaved roads	Vehicle-miles traveled	$5.9 \ \frac{s}{12} \ \frac{S}{30} \ \left(\frac{W}{3}\right)^{0.7} \ \left(\frac{w}{4}\right)^{0.5} \ \frac{d}{365}$	s = Silt content of aggregate or road surface material (%) S = Average vehicle speed (mph)
2. Paved roads	Vehicle-miles traveled	$0.09 \ I \ \frac{4}{N} \ \frac{s}{10} \ \frac{L}{1{,}000} \ \left(\frac{W}{3}\right)^{0.7}$	W = Average vehicle weight (tons) L = Surface dust loading on traveled portion of road (lb/mile)
3. Batch load-in (e.g., front-end loader, railcar dump)	Tons of material loaded in	$0.0018 \ \frac{\frac{s}{5} \ \frac{U}{5} \ \frac{h}{5}}{\left(\frac{M}{2}\right)^{2} \ \left(\frac{Y}{6}\right)} 0.33$	U = Mean wind speed at 4 m above ground (mph) M = Unbound moisture content of aggregate or road surface material (%)
4. Continuous load-in (e.g., stacker, transfer station)	Tons of material loaded in	$0.0018 \ \frac{\frac{s}{5} \ \frac{U}{5} \ \frac{h}{10}}{\left(\frac{M}{2}\right)^{2}}$	Y = Dumping device capacity (yd³) K = Activity factor[b]
5. Active storage pile mainte nance and traffic	Tons of material put through storage	$0.10 \ K \ \frac{s}{1.5} \ \frac{d}{235}$	d = Number of dry days per year f = Percentage of time wind speed exceeds 12 mph at 1 ft above the ground
6. Active storage pile wind erosion	Tons of material put through storage	$0.05 \ \frac{s}{1.5} \ \frac{d}{235} \ \frac{f}{15} \ \frac{D}{90}$	D = Duration of material storage (days) e = Surface erodibility (tons/acre/year)
7. Batch load-out (e.g, front-end loader	Tons of material loaded out	$0.0018 \ \frac{\frac{s}{5} \ \frac{U}{5} \ \frac{h}{5}}{\left(\frac{M}{2}\right)^{2} \ \left(\frac{Y}{6}\right)^{0.33}}$	P-E = Thornthwaite's Precipitation-Evaporation Index N = Number of active travel lanes
8. Wind erosion of exposed areas	Acre-years of exposed land	$3{,}400 \ \frac{\frac{e}{50} \ \frac{s}{15} \ \frac{f}{25}}{\left(\frac{P-E}{50}\right)^{2}}$	I = Industrial road augmentation factor[c] w = Average number of vehicle wheels h = Drop height (ft)

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a Represents particulate smaller than 30 µm in diameter based on particle density of 2.5 g/cm³.

b Equals 1.0 for front-end loader maintaining pile tidiness and 50 round trips of customer trucks per day in the storage area.

c * Equals 7.0 for trucks coming from unpaved to paved roads and releasing dust from vehicle underbodies;
* Equals 3.5 when 20% of the vehicles are forced to travel temporarily with one set of wheels on an unpaved road berm while passing on narrow roads;
* Equals 1.0 for traffic entirely on paved surfaces.

TABLE 2. PREDICTIVE EQUATION PRECISION FACTORS AND RANGES OF APPLICABILITY

Source category	Tested range of independent variable	Precision factor for 68% confidence interval
1. Unpaved roads	s: 4.3-68% S: 22-64 km/hr (13-40 mph) W: 3-142 t (3-157 T) w: 4-12 wheels	1.21
2. Paved roads	I: 1-7 N: 2-4 travel lanes s: 5.1-13.2% L: 42-629 kg/km (150-2,230 lb/mile) w: 3-12 t (3-13 T)	1.53
3. Batch load-in and load-out (e.g., front-end loader, railcar dump)	s: 1.3-7.3% U: 2.1-22 km/hr (1.3-14 mph) h: 1.5 m (5 ft) M: 0.25-0.7% Y: 1.5-7.7 m^3 (2-10 yd^3)	4.9
4. Continuous load-in (e.g., stocker, transfer station)	s: 1.9-19.1% U: 0.8-2.7 m/s (1.8-6.0 mph) h: 1.5-12 m (5-40 ft) M: 0.64-4.8%	5.4
5. Active storage pile maintenance and traffic	K: 1.0 s: 1.5% d: 235 days	[a]
6. Active storage pile wind erosion	s: 1.5% d: 235 days f: 15% D: 90 days	[a]
7. Wind erosion of exposed areas	e: 2.24 x 10^7 kg/km^2 yr (100 T/acre/yr) s: 8.5% f: 100% P-E: 40	[a]

Source: References 1, 2, and 3.

[a] Limited number of tests combined with theoretical development.

TABLE 3. SILT CONTENT VALUES APPLICABLE IN THE IRON AND STEEL INDUSTRY

Source	Number of tests	Range of silt content (%)	Average silt content (%)
Unpaved roads	12	4 -13	7.3
Paved roads	9	1.1-13	5.9
Material handling activities and storage pile wind erosion			
Coal	7	2 - 7.7	5.0
Iron ore pellets	10	1.4-13	4.9
Lump iron ore	9	2.8-19	9.5
Coke breeze	1	-	5.4
Slag	3	3.0- 7.3	5.3
Blended ore	1	-	15.0
Sinter	1	-	0.7
Limestone	1	-	0.4
Flue dust	2	14 -23	18.0

Source: Reference 3.

TABLE 4. SURFACE MOISTURE CONTENT VALUES APPLICABLE IN THE IRON AND STEEL INDUSTRY

Source	Number of tests	Range of surface moisture content (%)	Average surface moisture content (%)
Material handling activities and storage pile wind erosion			
Coal	6	2.8 -11	4.8
Iron ore pellets	8	0.64- 3.5	2.1
Lump iron ore	6	1.6 - 8.1	5.4
Coke breeze	1	-	6.4
Slag	3	0.25- 2.2	0.92
Blended ore	1	-	6.6
Flue dust	1	-	12.4

Source: Reference 3.

TABLE 5. SURFACE LOADING ON TRAVELED LANES OF PAVED ROADS IN IRON AND STEEL PLANTS

Number of tests	Range of surface loading (lb/mile)	Average surface loading (lb/mile)
9	65-17,000	2,700

Source: Reference 3.

the result that equation for unpaved roads is the most precise. By comparison, the one-sigma precision factor for paved roads is 1.53, while the two-sigma precision factor is 2.34 based on 10 tests.

To illustrate the effectiveness of the predictive emission factor equation for unpaved roads, comparisons may be made between predicted emission factors and the corresponding measured values in the supporting data base.[2] As shown in Figure 1 (Case 3), the measured emission factors for unpaved roads, which span two orders of magnitude, are predicted using the emission factor equation with a two-sigma precision factor of 1.46, i.e., the 95% confidence interval for a predicted emission value, P, extends from P/1.46 to 1.46 P. If the average of all emission factor measurements is used instead of the equation, the two-sigma precision factor escalates to 5.2. In the other case shown in the figure, the average of measurements at a given site predicts the measurements at that site with a precision factor of 2.3.

The one-sigma precisions of the equations for batch and continuous material handling are 4.9 and 5.4 based on 8 and 9 tests, respectively. The diversity of materials handled and handling operations necessitates that more tests be performed and that the predictive equations be modified to achieve a higher degree of precision. However, the measured emission factors for typical material handling operations indicate that these operations are small sources in most industrial settings and may not merit further testing.

The precision factors for the storage pile maintenance, storage pile wind erosion and exposed area wind erosion equations are unknown since only limited testing of these sources has been performed to date. Wind erosion is currently being investigated by MRI using a portable wind tunnel with the goal of developing a statistically precise predictive emission factor equation for the wind erosion of storage piles and exposed areas.

EFFICIENCIES OF OPEN DUST SOURCE CONTROLS

Only limited testing results are available to define the efficiencies of various open dust source control techniques. However, MRI is currently engaged in a project funded by the U.S. Environmental Protection Agency (EPA Contract No. 68-02-3177, Task 4) and entitled "Iron and Steel Plant Open Source Fugitive Emission Control Evaluation," which is directed to the quantification of control efficiencies for open dust sources.

In the absence of adequate test data on control efficiency, the predictive equations shown on Table 1 can be used to estimate control efficiencies, if the changes in the independent variables affected by these control techniques can be quantified. Table 6 identifies the independent variables in the predictive equations in Table 1 which are affected by various open dust source control techniques.

Table 7 shows the results of 8 control technique quantification tests for emissions from unpaved roads. Two tests were performed on roads treated with Coherex® (petroleum resin), three on roads treated with TREX (ammonium lignin-sulfonate), and two roads were tested after a precipitation event.

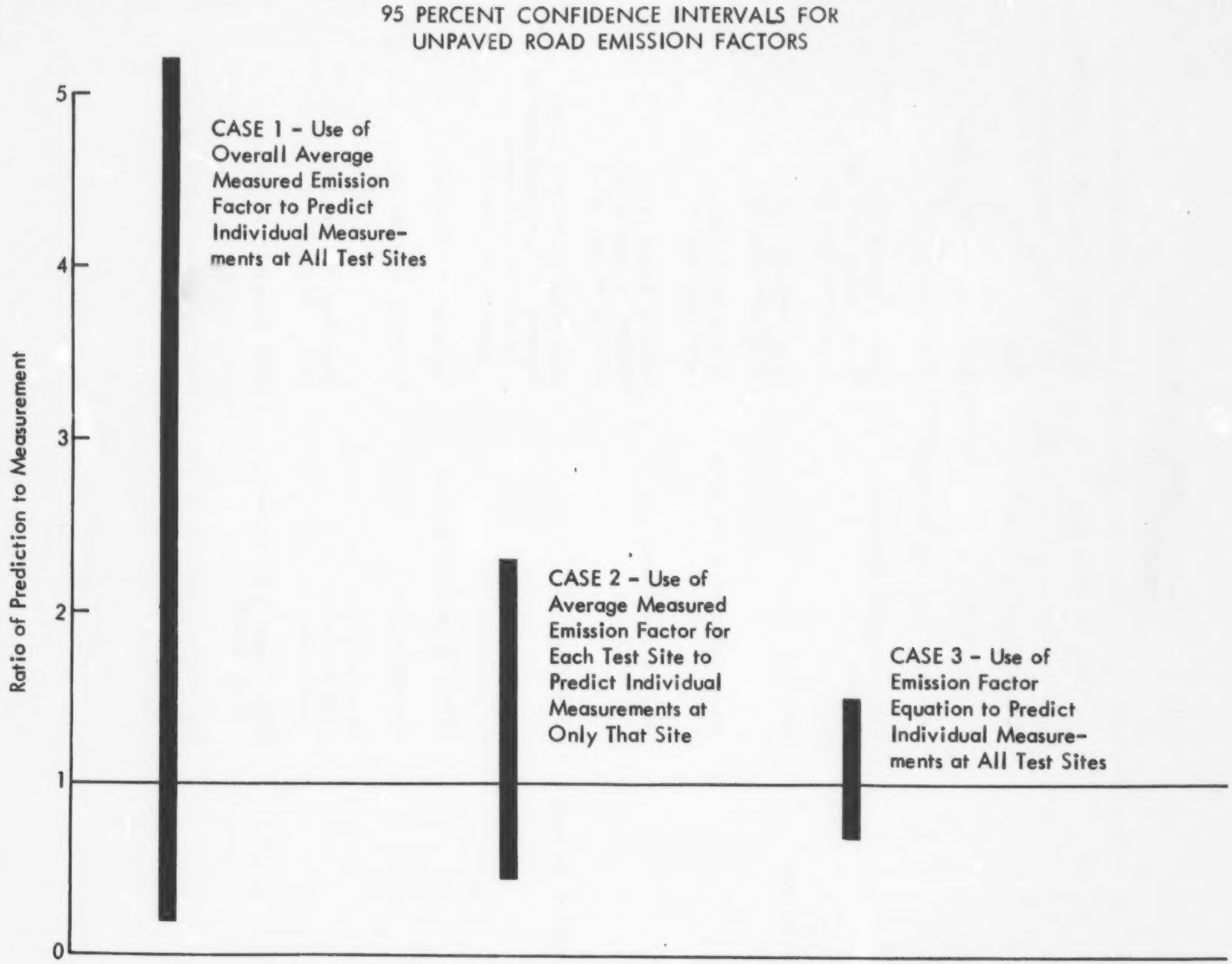

Figure 1. Comparison of unpaved road emission factor precisions.

TABLE 6. EFFECT OF CONTROL TECHNIQUES ON INDEPENDENT VARIABLES

Source	Control technique	Independent variable affected
Unpaved roads	Watering (anthropogenic)	None[a]
	Precipitation	Number of dry days (d)
	Chemical dust suppressants	Silt content (s)
	Vehicle speed and type control	Vehicle speed (s) Number of wheels (w) Vehicle weight (W)
Paved roads	Flushing	Silt content (s) Total loading (L)
	Broom and vacuum sweeping	Silt content (s) Total loading (L)
	Vehicle speed and type control	Vehicle speed (s) Number of wheels (w) Vehicle weight (W)
Material handling	Windbreaks	Mean wind speed at 4 m (U) Percent of time wind exceeds 12 mph at 1 ft above eroding surface (f)
	Watering (anthropogenic)	Moisture content (M)
	Precipitation	Moisture content (M)
	Chemical dust suppressants	
	Water extenders	Moisture content (M)
	Agglomerators	Silt content (s)
	Reduce aggregate material drop height	Drop height (h)
	Use larger capacity equipment for batch handling	Dumping device capacity (Y)

TABLE 6. (continued)

Source	Control technique	Independent variable affected
Wind erosion of storage piles	Watering (anthropogenic)	None[a]
	Precipitation	Number dry days (d)
	Chemical dust suppressants	Silt content (s)
	Windbreaks	Percent of time wind exceeds 12 mph at 1 ft above eroding surface (f)
	Crusting of inactive piles (induced by watering, precipitation, and chemical suppressants)	Silt content (s)
Wind erosion of exposed areas	Watering (anthropogenic)	None[a]
	Precipitation	PE Index (PE)
	Chemical dust suppressants	Silt content (s) Erodibility (e)
	Windbreaks	Percent of time wind exceeds 12 mph at 1 ft above eroding surface (f)
	Crusting of inactive surfaces (induced by watering, precipitation, and chemical dust suppressants)	Silt content (s) Erodibility (e)

[a] Watering does not affect silt content since s is determined by dry sieving.

TABLE 7. SUMMARY OF CONTROL EFFICIENCY TESTS FOR UNPAVED ROADS

Road surface	Uncontrolled emission factor (lb/VMT)	Control type	Time after chemical application or rainfall cessation (hrs)	Measured Controlled emission factor (lb/VMT)	Control efficiency (%)
Dirt/slag	2.3 (M)[a]	10% Coherex® in water	20	0.073	97
		10% Coherex® in water	22	0.36	84
Crushed rock	21.5 (P)	25% Trex in water; 0.1 gal/yd^2	24	2.0	91
			26	2.3	89
			27-1/2	3.6	83
Crushed rock & glacial till	21.6 (M)	Rainfall of 1.13 in. on two preceding days	23	2.3	89
Crushed lean taconite rock	21.5 (P)	Rainfall of 1.13 in. on two preceding days	28-1/2	11.6	54
			29-1/2	11.6	54

Source: References 2 and 4.

[a] M = measured

[b] P = predicted

Consistent with the emission factor equation for unpaved roads, the lowering of emissions on the Coherex-treated road was reflected by a reduction in silt content from 9.0% to 0.03%.

It is evident from Table 7 that in all cases the decay in control efficiency with time after application and road usage was dramatic. The control efficiency of Coherex decayed from a high initial value (exceeding 90%) to 84% efficiency within 22 hr after application, while TREX similarly decayed to 83% efficiency within 27-1/2 hr after application. The natural control of precipitation decayed to 54% within 29 hr after the rain ended.

CONCLUSIONS

Emission factor equations which are applicable to uncontrolled open dust sources in iron and steel plants have been developed and are being improved through the generation of a more extensive and reliable data base. The use of predictive emission factor equations provides for much greater precision than single-valued emission factors by incorporating correction parameters which account for source variability. Presently, the equations for the two open dust sources of greatest magnitude (unpaved and paved roads) have good precision, with one-sigma precision factors of 1.21 and 1.53 for unpaved and paved roads respectively. The tested ranges of independent variables which enter into the equations generally encompass the uncontrolled source conditions found at iron and steel plants.

The lack of quantitative data on open dust source control efficiencies indicates a strong need for more source testing. As an interim measure, the predictive emission factor equations may be used to estimate control efficiencies. This entails the measurement or estimation of the independent variables under controlled conditions rather than the more difficult measurement of the reduction in particulate emissions.

Limited testing of chemical dust suppressants for industrial unpaved roads indicates a high initial control efficiency (exceeding 90%) which decreases by more than 10% within about 24 hr after application. Consistent with the emission factor equation, the lowering of emissions is reflected by the reduced silt content of the road surface material after the application of chemical dust suppressants. Additional testing is needed to better quantify the performance of road dust suppressants.

ACKNOWLEDGEMENT

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ENGLISH TO METRIC UNIT CONVERSION TABLE

English unit	Multiplied by	Metric unit
lb/T	0.500	kg/t
lb/vehicle mile	0.282	kg/vehicle km
lb/acre yr	112	kg/km^2 yr
lb	0.454	kg
T	0.907	t
mph	0.447	m/s
mile	1.61	km
ft	0.305	m
acre	0.00405	km^2

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WIND VELOCITY DISTRIBUTION OVER STORAGE PILES AND USE OF BARRIERS

by

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ABSTRACT

To reduce the wind blown dust from storage piles of coal or other bulk materials, wind tunnel tests of scale models are being made to determine the effect of pile configuration and use of wind barriers to reduce wind penetration.

Preliminary results show that a wind break or barrier simulating a snow fence whose height is 1/2 the pile height with a solidity of 2/3 may reduce the penetration velocity of wind by one-half when it is placed three pile-heights away as an optimum. A similar barrier of 1/4 pile height located 2.5 pile-heights away reduces the wind velocity by 23 percent. The effect of leeward barriers is less obvious, however. Reduced wind penetration into a pile also conserves the moisture in the pile thus improving the adhesion of dusts.

NOMENCLATURE

SYMBOLS

C_p	Pressure coefficient
h	Height of pile
k_p	Permeability of a pile, m^2
L	Characteristic length, m
N_{Re}	Reynolds number, dimensionless
P	Pressure, Pa
V	Wind velocity, m/s
ρ	Density of fluid, kg/m^3
μ	Viscosity of fluid, kg/ms

Subscripts

o	Characteristic or freestream quantitites
p	Quantities inside the pile

INTRODUCTION

The significance of the abatement of fugitive emission the form of wind blown dust from storage piles of bulk materials such as coal and ores is seen from the measurements reported by Cowherd and Hendricks (1977)[1]. The annual wind loss of particles below 30 μm size from a single steel plant may run into thousands of tons from storage piles alone. Nationally, this mode contributes to 10 percent of total suspended particle emissions of particles below 30 μm (Cowherd, et al. 1979)[2] thus constituting an important pollution source. Estimated typical control efficiency is around 40 percent.

Many factors influence this wind erosion loss such as wind velocity, moisture content, rainfall, duration of storage, compaction of pile and the amount and size of fines, and the pile configuration. To this, we may add the effectiveness of means of abatement. Wind erosion tests were made in wind tunnels to simulate both stationary piles and rail cars (Nimerick, et al 1979)[3]. Similarity relations are, however, complicated in that wind velocity distribution over a pile is affected by the characteristic Reynolds number of the pile while the lifting of particles from a pile is influenced by the size of particles and shear flow (Soo and Tung 1972)[4].

The present research concerns abatement of such a pollution source as well as conservation of resources. The task consists of quantification, simulation, and optimization of the shape and orientation of a porous storage pile and the strategic use of economically feasible barriers (windbreaks) or covering. The desirable condition includes minimum penetration at the windward end of the pile by dynamic pressure and the leeward end of the pile by separated flow and trailing vortices. This part of the study has been made by wind tunnel testing and numerical modeling of the fluid mechanics involved in wind penetration. The results will facilitate prediction of the behavior of the dust plume. This will lead to the desirable external protection and pile configuration and orientation and accurate estimation of dust production by wind based on the characteristics of particles.

To insure accurate prediction, strict modeling criteria have been followed.

SIMILARITY RELATION

Similarity of flow over a porous specimen or model to that of the prototype storage pile is achieved by keeping their characteristic Reynolds numbers equal. The latter is given by:

$$N_{Re} = L_o \rho V_o/\mu$$

where L_o is a characteristic length such as pile height, V_o is the characteristic wind velocity, ρ and μ are the density and viscosity of air, respectively. For the present study, control of the boundary layer thickness of the approaching flow is also needed. Typical relations are seen in the following example:

	Prototype	Model
Pile Height	3.05 m	76 mm
Air Velocity (V_o)	1.14 m/s	46 m/s

Because of the large wind velocity needed in the model for similarity, the above pile of simulating bulk material has to be confined by a wire screen.

Similarity in wind penetration into a porous pile is characterized by a parameter which is the ratio of viscous resistance to external freestream to the resistance to flow through the pores:

$$\mu L_o/k_p \rho V_o$$

where k_p is the permeability of the pile given by the Kozeny-Carman relation (Carman 1956)[5]: $k_p = \varepsilon^3/S^2 \alpha$, where ε is fraction void called porosity, S is the surface area per unit volume, and α is constant which is nearly 5. The basis of choosing k_p is given by the relation for the flow velocity in the porous body V_p is given by:

$$V_p = (k_p/\mu) \nabla P$$

where ∇P denotes gradient of pressure in the porous body. For similar materials and chips of coal of similar size distributions, typical size relations are:

Prototype: 10 x 0 cm; Model: 2.54 x 0 mm (No. 8 Sieve)

EXPERIMENTAL FACILITY

For the quantitative modeling of a coal pile under the influence of wind, our present multiphase wind tunnel facility of 305 mm square cross-section have been modified to accommodate a specimen as in Figure 1 showing traversing stations. This device makes possible testing of two-dimensional porous specimens, simulating a coal pile. Wind velocity distributions are determined by traversing of pitot-static and yaw probes outside of the pile model. From these measurements, penetration of wind into the inside of the pile was deduced.

Models were designed to simulate prototype storage piles. Field observation of storage piles of coal was made by J. D. Tyrrel at the Consumer Power Company, J. C. Weadock Plant, Essexville, Michigan. Measurements from photographs taken gave angles of 37.4 and 37.7 degrees from the horizontal. These coal piles had an average height of 3.05 m (10 ft). Variables affecting coal pile configurations and packing frequencies were amount and frequency of coal supply, area of coal pile, coal usage demands, hopper location, stacking capabilities, and manpower.

Based on these observations, a 76 mm and a 51 mm thick porous piles of haydite* 305 mm wide and 610 mm long (base) were prepared with pile angles of 40 and 35 degrees on the two ends for the preliminary measurements. These models can be reversed in the wind tunnel to test effects of pile angles.

Preparation of the porous specimen included crushing solids, haydite (sp. gr. 1.31) in this case, to the desired sizes followed by sieving and mixing to achieve the desired porosity for the purpose of simulation.

A 3 mm square wire screen has been used to cover the particles of 3 mm by 6 mm to maintain the prescribed geometry and porosity. This screen cover is needed because of the high wind velocity used in the simulation. The pile has a porosity (void) of 0.40 and a permeability of 1.77 x 10^{-8} m^2.

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*A high grade shale product which is kiln processed and crushed to nearly 10 mm size.

Figure 1 shows that for each given particle size constituting the bulk of the pile, the variables of geometry are the height (h), length (L), and angles (θ_1 and θ_2) of the pile. Simulation of actual wind profiles is accomplished by a long inlet pipe length to give a fully developed boundary layer. Standard pitot and yaw probes were used with fluid and electronic manometers. A hot wire anemometer was used to determine the velocity fluctuations.

Figure 1 also shows the model and the stations at which air velocity was measured. At stations A through I, a pitot probe was inserted vertically to determine the flow configuration surrounding the pile. At points 1 through 11, the yaw probe was inserted horizontally in order to measure the air velocity and angle at the surface of the pile.

For these experiments, average wind velocities were chosen by damper adjustment and fan speed.

Type of barriers tested include 25.4 mm barriers, solid and slotted to a solidity of 2/3, and 13 mm barriers, solid and slotted to 2/3 solidity. All these were tested for optimum locations ahead of the pile (windward) and behind the pile. All locations are in terms of nominal pile heights.

When testing the 51 mm pile model, the 25.4 mm barrier corresponds to 1/2 the pile height in order to simulate a likely real situation. The objective was to simulate simple fences that could be used as a means to reduce wind penetration and lift of dust. In all cases, the barriers were set parallel to the front or back edge of the pile and perpendicular to the bottom plate of the wind tunnel.

MEASUREMENTS AND EXPERIMENTAL RESULTS

Tests have been made principally with a pile of 51 mm height and a pile of 76 mm height. Extensive measurements have been made both to determine the reference condition of flow over the pile with an inlet boundary layer simulating the atmospheric wind tests were made first without protective barriers and subsequently with various forms of barriers.

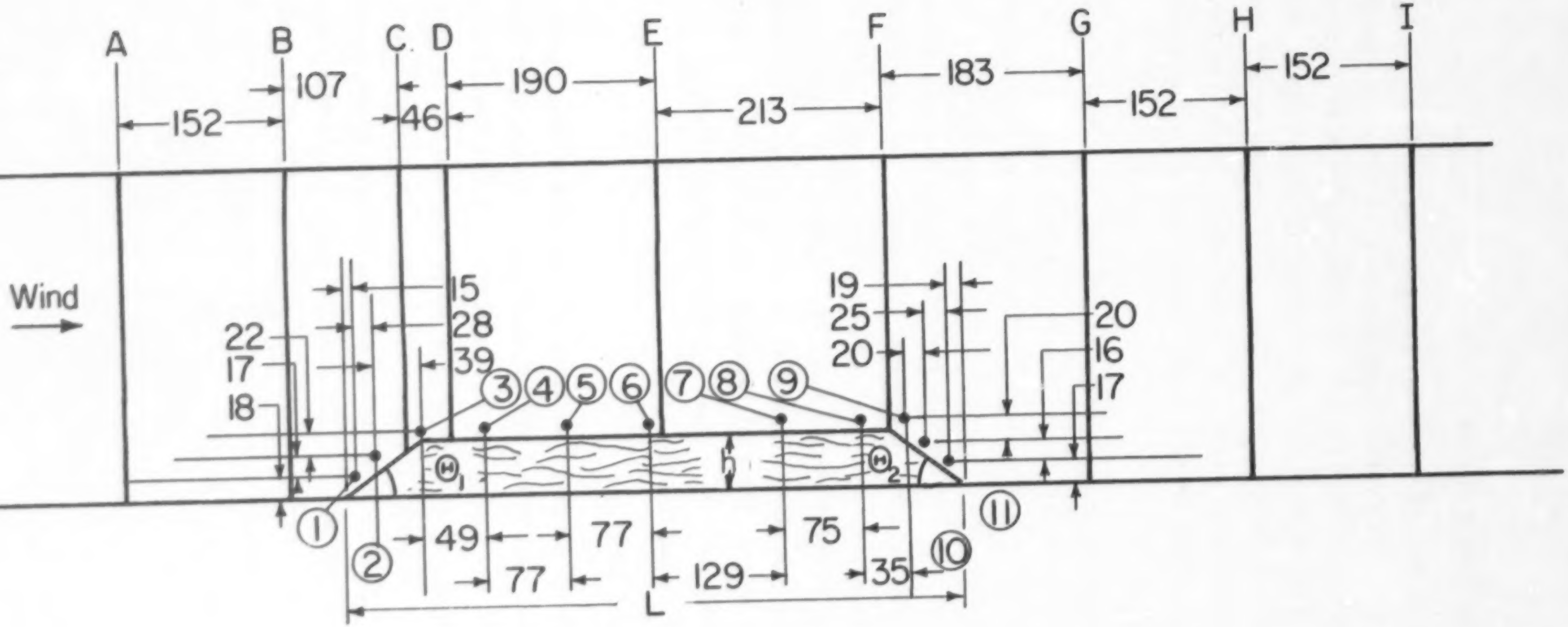


Figure 1 Measuring stations of wind velocity over the porous specimens (all dimensions in mm)

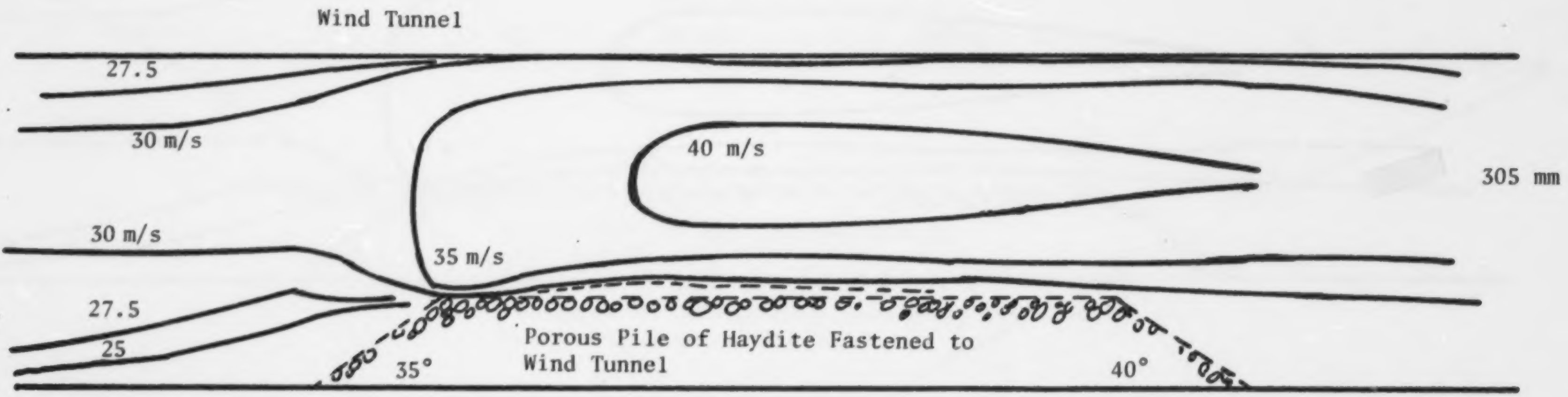
1. Tests without Barriers

A typical set of test results is shown in Figure 2. Figure 2a shows the wind velocity contour over the pile in the wind tunnel at a nominal wind velocity of 30 m/s based on pitot static tube traverses. Figure 2b shows the result of a yaw prove survey giving velocity and direction of wind in the vicinity of the pile. The increase in air velocity above the pile needs correction for comparison to free flow above ground. Figure 2 provides for a general understanding of the flow field around a pile.

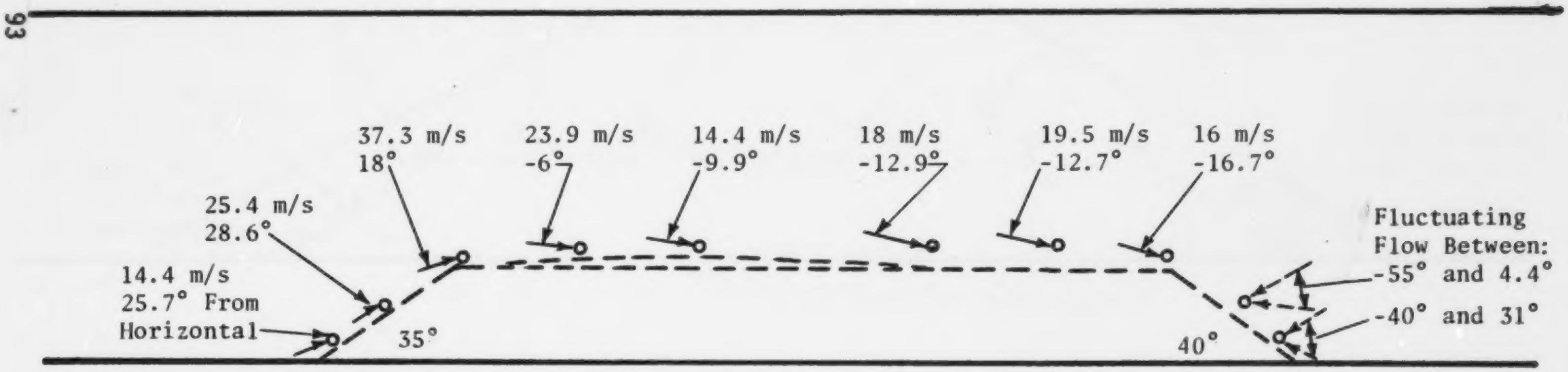
Detailed typical measurements in Figure 3 show the evolution of the air velocity profile around the porous pile specimen. As is readily seen, Fig. 3 shows a typical turbulent flow profile for the approaching flow. Velocities at stations D through G represent clearly the regions where separation of the flow occurs while velocities at stations G and H show the reattachment at the boundary layer. Figure 4 shows the results of traverse across the pile specimen with the velocity profiles of the flow at the testing points near the surface. It should be noticed that even when the limits of the regions of flow separation cannot be exactly determined due to the finite number of probe points, these separation zones appear clearly defined by zero velocity readings at the surface of the pile as shown in Figure 3.

2. Windward Barriers

The use of barriers in front of the pile model appear to be the simplest way to control wind penetration. In order to test how effective this method is, two kinds of barriers of two different heights were tested (solid and slotted). The probe was placed, in turn, at stations 3 and 9 (see Figure 1) which were located in regions where flow penetration was likely to occur. At those points, the air velocity was measured at different distances from the front glass of the tunnel and the barrier was placed at different distances from the edge of the pile. The experimental results for a solid barrier placed in front of the pile model are shown in Figure 5.



(a) Air Velocity (Horizontal Component) Over the Porous Pile-Pitot Static Tube Survey



(b) Flow in the Vicinity of Pile-Yaw Probe Survey

Figure 2 Wind tunnel measurement of flow over and into a 76 mm high porous pile

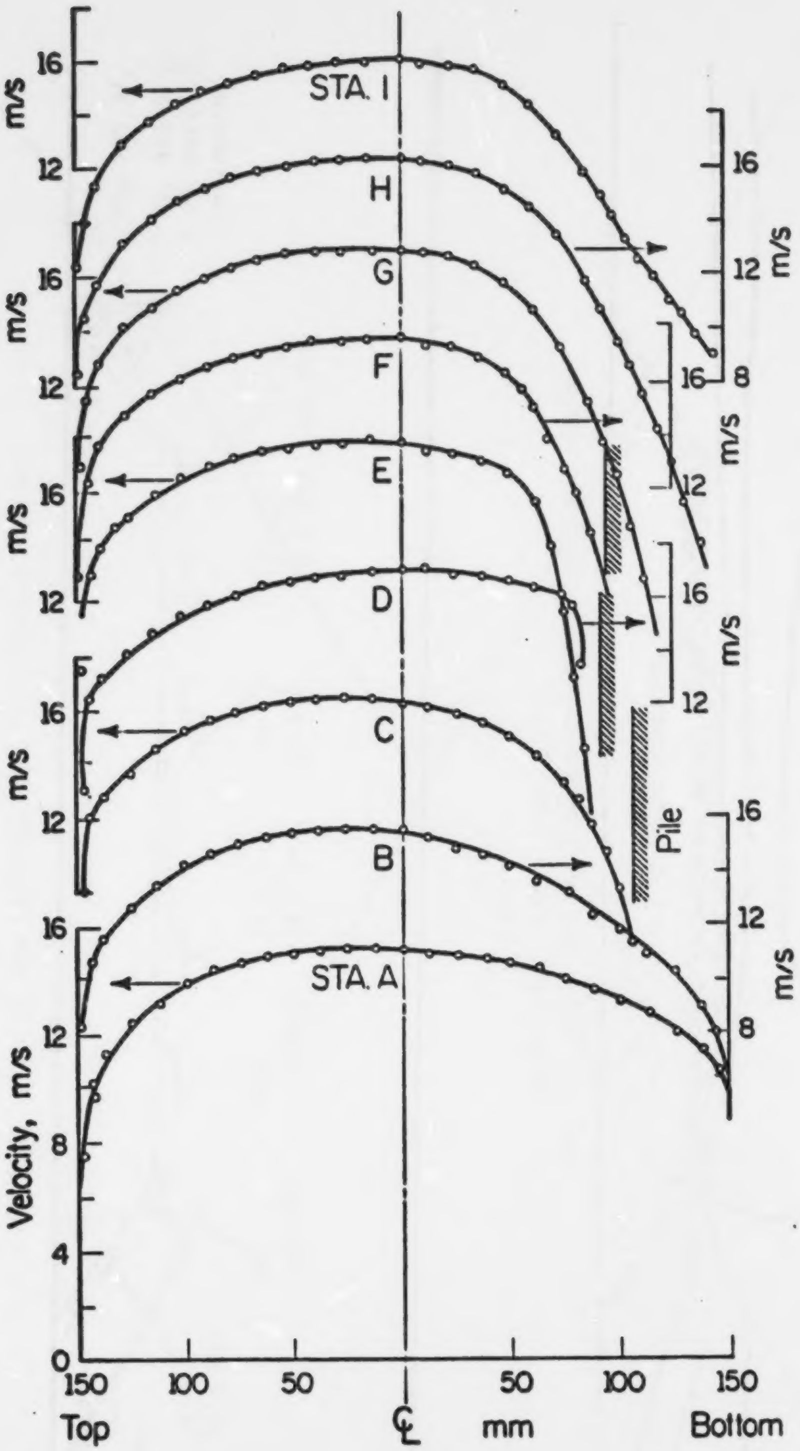
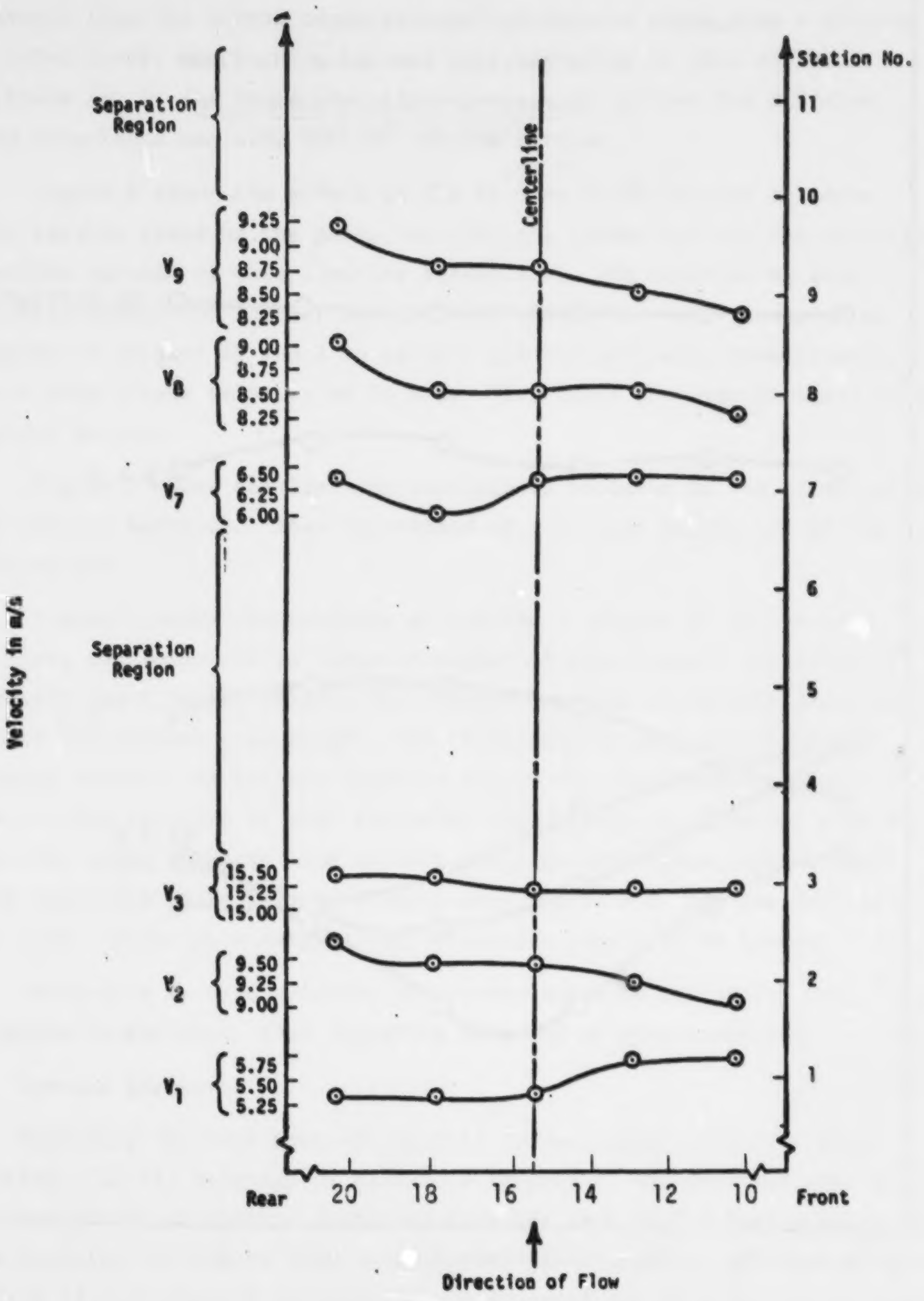


Figure 3 Typical air velocity distribution over a porous pile



(Positions in cm from front glass)

Figure 4 Flow velocity over the porous pile from horizontal traverses

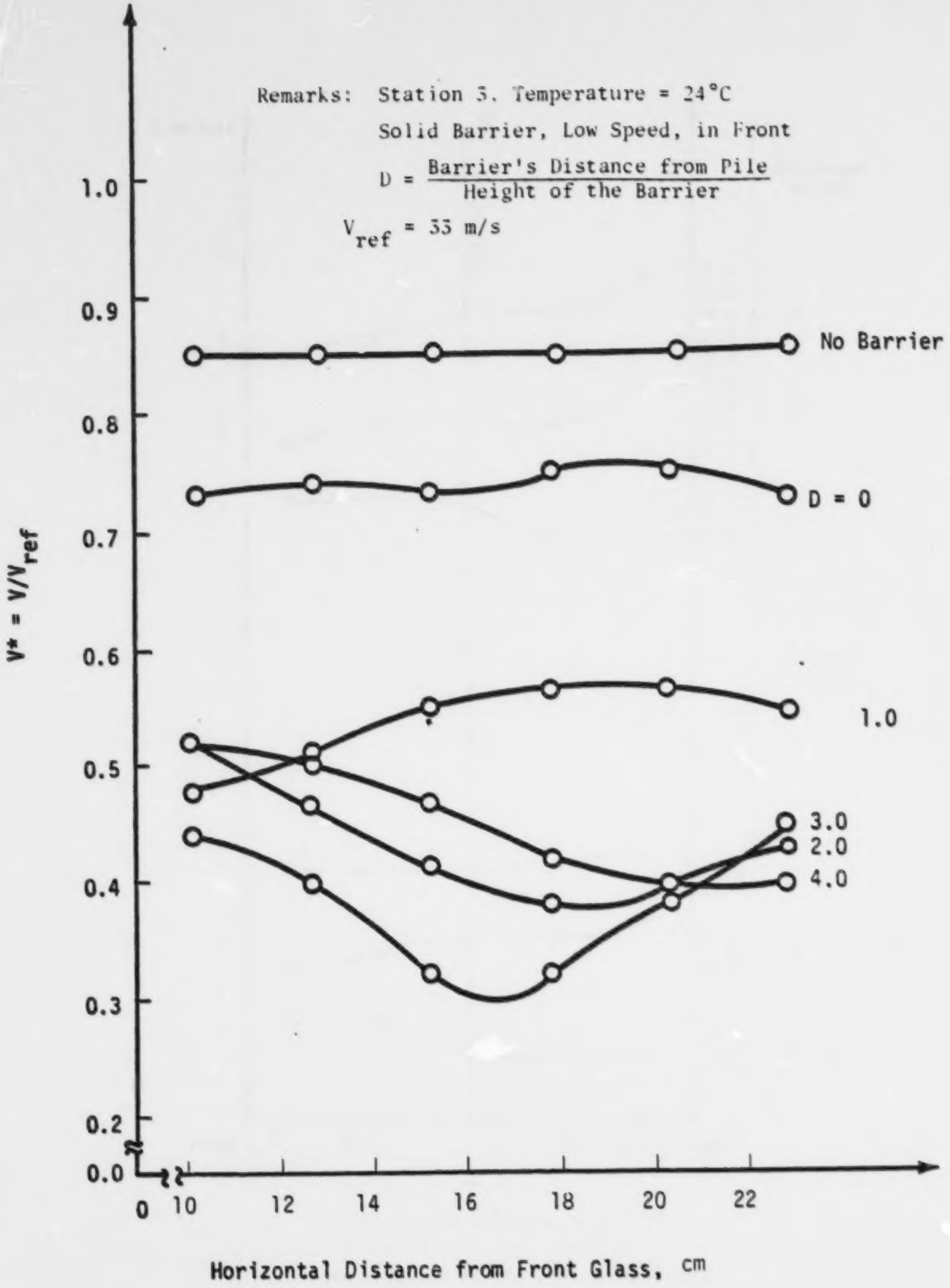


Figure 5 Velocity profile in the horizontal plane at various forward barrier locations

It is seen that at a distance equivalent to three pile heights measured from the bottom edge, the air velocity at point 3 is a minimum. In other words, the barrier becomes most effective at this distance. Furthermore, it was found that this distance is optimum for different wind velocities and also for the slotted barrier.

Figure 6 shows the effect of the 25.4 mm solid barrier at three pile heights ahead of the pile, the limiting streamline and the velocity profiles outside of this limiting streamline. The fluctuating wind velocity behind the barrier was measured with a hot wire anemomter at stations 1 (Figure 1) and 2 to be 12.7 m/s and 10.6 m/s, respectively, for a free stream velocity of 33 m/s. This shows the effectiveness of a forward barrier.

Figure 7 shows the limiting streamlines produced by the 13 mm solid and slotted barriers. They correspond to a barrier height 1/4 of the pile height.

Figure 8 shows the velocity at station 3 (Figure 1) for various barriers and locations in terms of number of pile-heights for solid barriers and 2.5 pile-heights for slotted barriers of heights equal to 1/4 of the nominal pile-height, and three pile-heights for solid and slotted barriers of heights equal to 1/2 of the nominal pile-height. The scaling relation is that the model corresponds to an actual pile of 3 m high under 20 km/hr wind and a 1.5 m high snow fence reduces the wind approaching the pile to 9 km/hr when placed 9 m from the foot of the pile. Other pile heights and velocities remain to be tested.

Reduction in wind velocity also contributes to conserving the moisture in the pile, thus improving adhesion of fine particles.

3. Leeward Barriers

Expecting the back part of the pile to be a region for flow penetration, the air velocity at station 9 (Figure 1) was measured with a barrier placed at various distances from the back edge. Test results of the downwind barrier to this stage appears inconclusive, although nondetrimental if the windward barriers become downwind due to a reverse in wind direction.

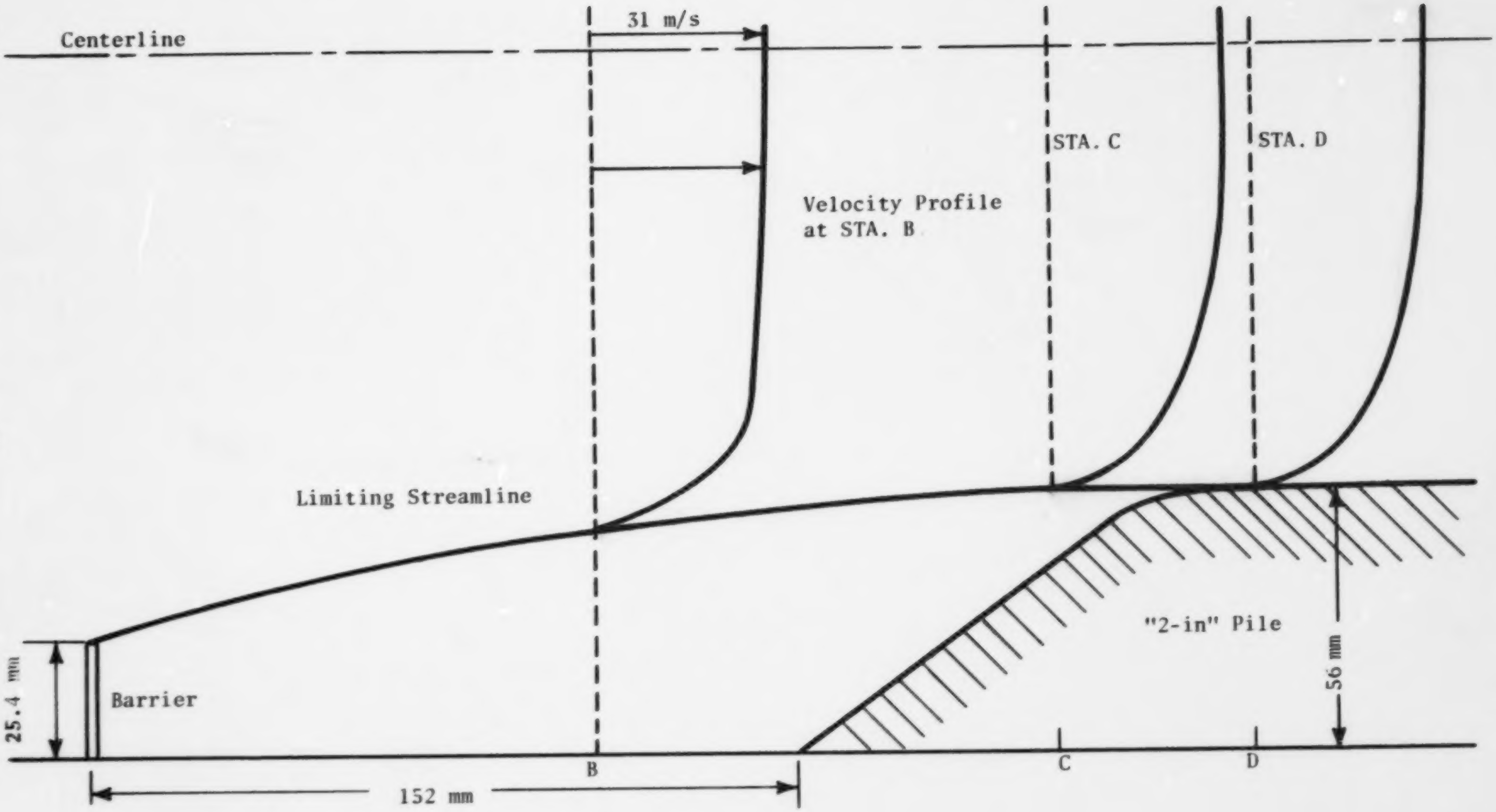


Figure 6 Velocity profiles and limiting streamline for flow over a 25.4 mm barrier located at three pile heights in front of the pile

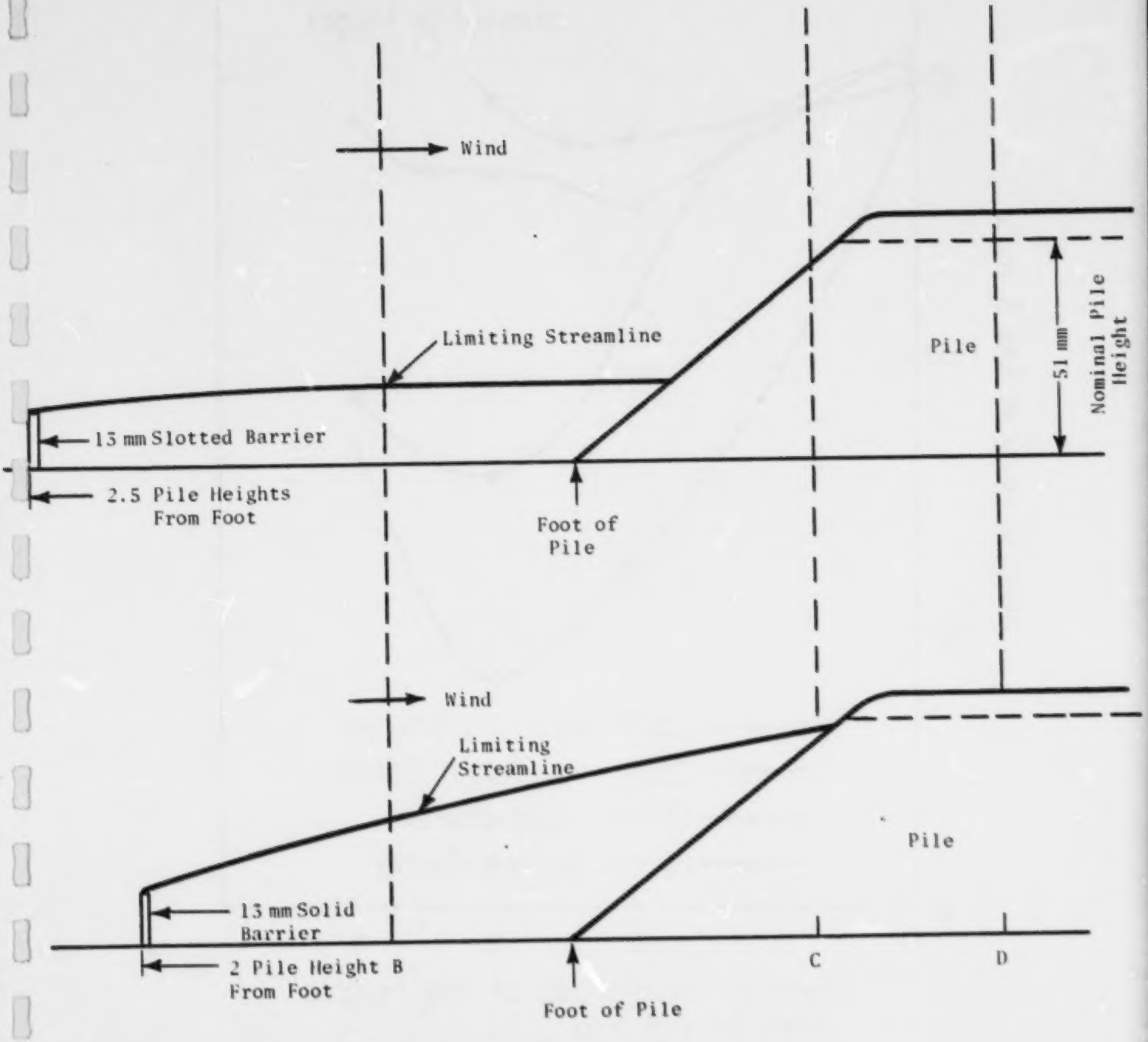


Figure 7 Limiting streamlines for barriers of 1/4 nominal pile height near optimum locations (velocity along centerline of duct is 31 m/s)

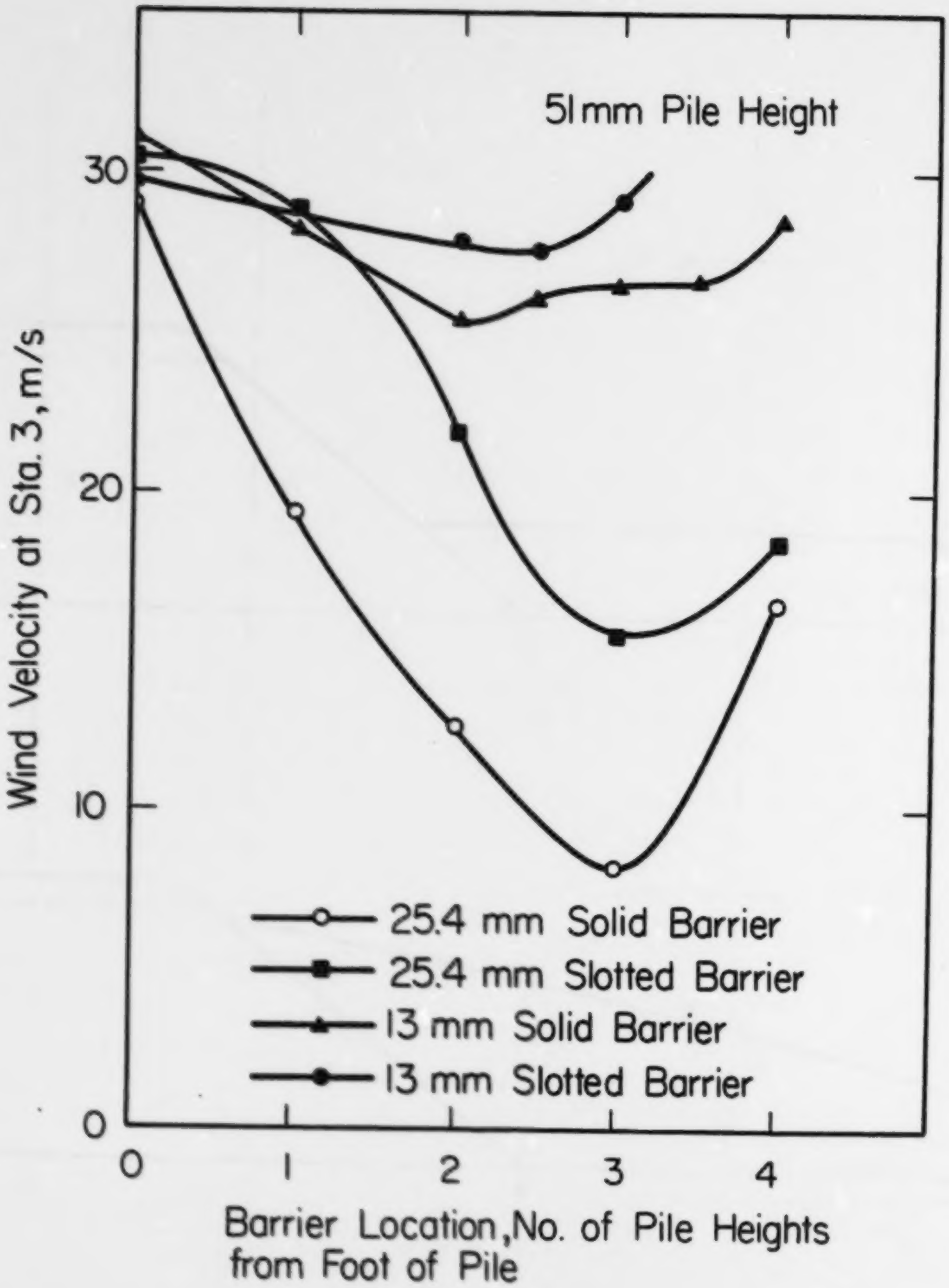


Figure 8 Effect of windward barrier location in reducing wind penetration--station 3

Figure 9 shows the limiting streamlines of flow separation for the condition of no barrier (solid line) and the wind velocity distribution, the use of 25 mm solid barrier (dotted lines for the barrier and the limiting streamline) and the use of 13 mm solid barrier (dashed lines for the barrier and the limiting streamline).

Figure 10 shows the wind velocities at stations 9, 10, and 11 for 25 mm solid barrier at various pile heights from the foot of the pile.

DISCUSSION

Experimental study to this stage shows that, wind barriers such as snow fences, when properly deployed, can reduce wind penetration into a storage pile by one-half. This reduces blowing of dust as well as loss of moisture from the pile. Loss of moisture tends to increase the amount of fine dust in loose form. It appears desirable to have the length of a pile normal to prevailing wind, with snow fences along both sides.

It appears that wind loss of dust from storage piles occur in three modes (2): blowing due to wind penetration, erosion of the flat top as an effective exposed area, and during load-in and load-out. The first two modes occur over long durations. Wetting down with water as a dust suppressant and reducing wind penetration will reduce the loss significantly. The eventual computer program will include estimation of loss of dust and dispersion according to existing models. The former concerns entrainment and blowing of dust from the passages of the porous pile (Soo 1967, Settari 1975)[6,7] and the latter concerns diffusion of dust plume from nonpoint areas (Neuman 1975)[8]. These will also be covered in future tests. An input to the emissions factor equations such as in Cowherd, et al. (1979)[2] is expected with the presence of barriers.

Application of coating or other dust suppressant on storage piles is also within consideration. Economic justification and cost effectiveness of protective devices are essential.

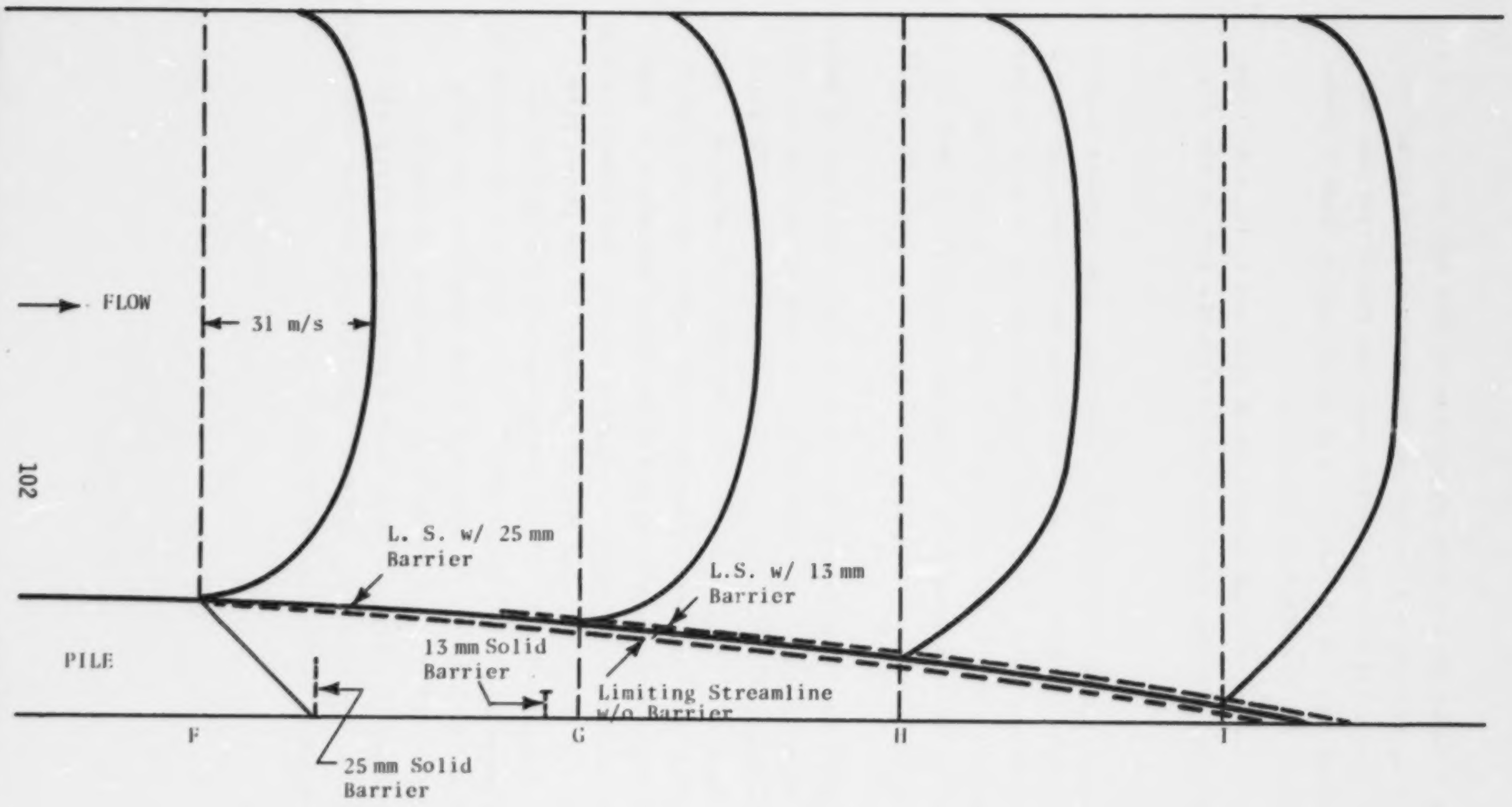


Figure 9 Limiting streamlines for flow downwind of the storage pile for the conditions of: without a barrier, with a 13 mm solid barrier, and a 25.4 mm solid barrier. Velocity profiles are for the case without a barrier.

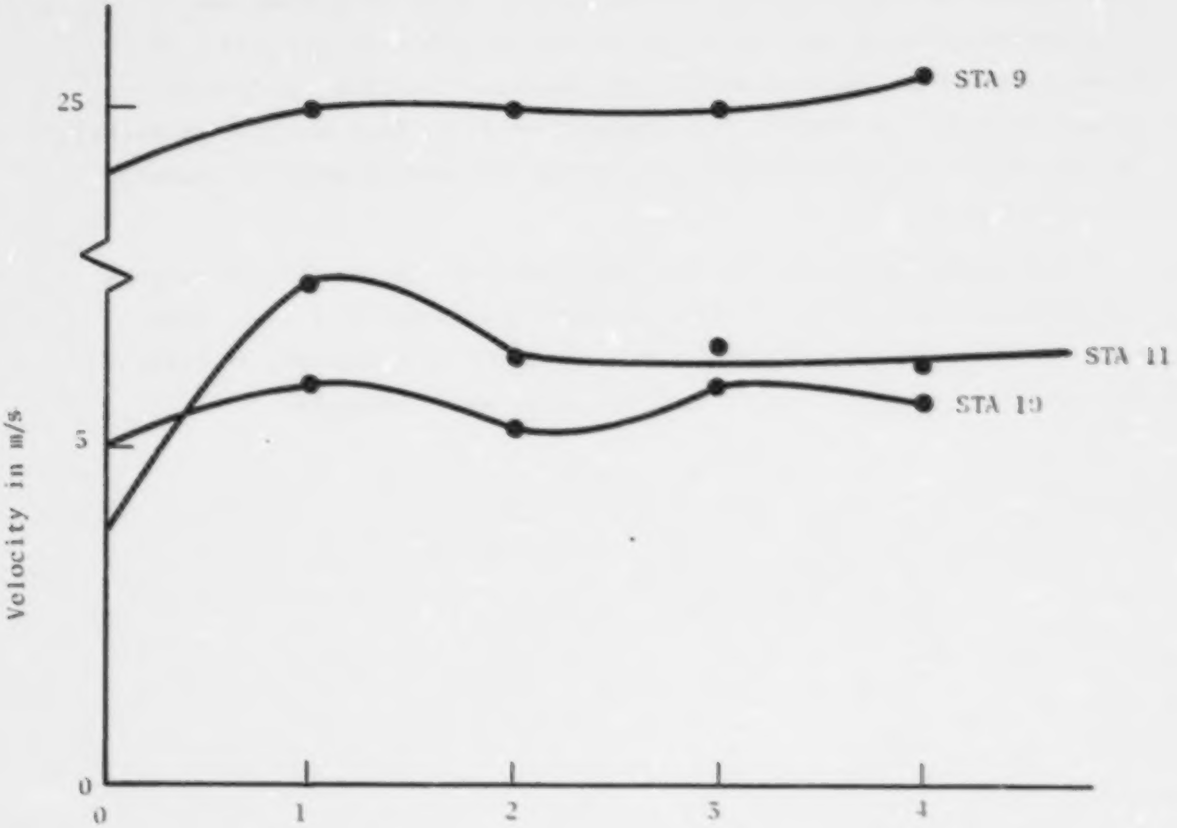


Figure 10 Effect of leeward barrier (25.4 mm solid barrier) location on wind velocity behind the pile (STA's in Fig. 2)

CONCLUSIONS

To this stage of an experimental program, we conclude, in a preliminary sense, that barriers such as snowfences or height 1/4 to 1/2 of that of the storage pile, if properly deployed in the windward direction of the pile at two to three pile heights away, can reduce the wind penetration and the resulting lift of dust by 25 to 60 percent,not counting the reduced rate of drying of the materials in the pile. If these barriers are located also in the downwind location, no harmful effect is noted. A tentative recommendation is to have the pile protected in the directions of prevailing wind as an inexpensive means of reducing wind blown dust.

Continuing study will include the effect of changes in pile heights and geometry (angles, etc.), pile porosity and amount of fines. Wind velocity patterns behind a windward barrier and in front of a trailing barrier will be studied in detail with a hot wire anemometer.

ACKNOWLEDGEMENTS

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PARTICULATE AND SO_2 EMISSION FACTORS FOR HOT METAL DESULFURIZATION

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INTRODUCTION

The Source Evaluation and Analysis Division (SEA) of Acurex Corporation undertook a series of tests for EPA Region 5 at the hot metal desulfurization plant of Kaiser Steel located in Fontana, California. The tests were performed to develop emission factors (particulate mass, particle size, SO_2) for uncontrolled and controlled emissions from this process.

PROCESS DESCRIPTION

Kaiser Steel owns and operates an external hot metal desulfurization (HMDS) plant at its Fontana Works located in Fontana, California. The plant began operation in the spring of 1978 and uses technology based on the Nippon Steel Corporation desulfurization process. Hot metal from the blast furnace arrives at the HMDS plant in torpedo cars which are rolled into a partially open shed attached to the HMDS building. Lances with stoppers are inserted into as many as three torpedo cars at one time and a predetermined amount of calcium carbide (CaC_2) and calcium carbonate ($CaCO_3$) is blown into the hot metal using nitrogen (200 cfm at 30 to 40 psi). The calcium reacts with the sulfur in the metal to form a slag which floats to the top of the torpedo car. The hot metal is usually desulfurized to <0.03 percent sulfur but can be reduced to as low as 0.003 percent sulfur for special low sulfur steel production. The stopper on the lance fits into the mouth of the torpedo car to minimize emissions during the desulfurization process which lasts approximately 8 to 16 minutes. Emissions which do escape around the stopper are captured by a local hood and ducted to a six compartment, positive pressure Wheelabrator-Frye baghouse. The design capacity of the baghouse is 100,000 scfm and it contains 1728 Dacron bags, each 5.25 inches in diameter and 14 feet 3 inches long. The air-to-cloth ratio of the unit is 3:1 at a design pressure drop of 7 to 8 inches w.g. Bag cleaning is accomplished by mechanical shaking and the cleaned gases are exhausted to the atmosphere via six stacks -- one for each compartment. The dust collected by the baghouse (~2 tons per day) is trucked to landfill for disposal. After desulfurization is complete the torpedo cars are taken to the skimming station of the Basic Oxygen Plant (BOP) where the slag is skimmed from the hot metal. This hot metal is now suitable for use in the Basic Oxygen Furnace (BOF).

SAMPLING LOCATIONS

Uncontrolled Emissions Location

Samples of the uncontrolled emissions from the HMDS process were collected at the inlet to the baghouse as indicated in Figure 1. The particle size sampling ports (six total, three equidistant ports on each

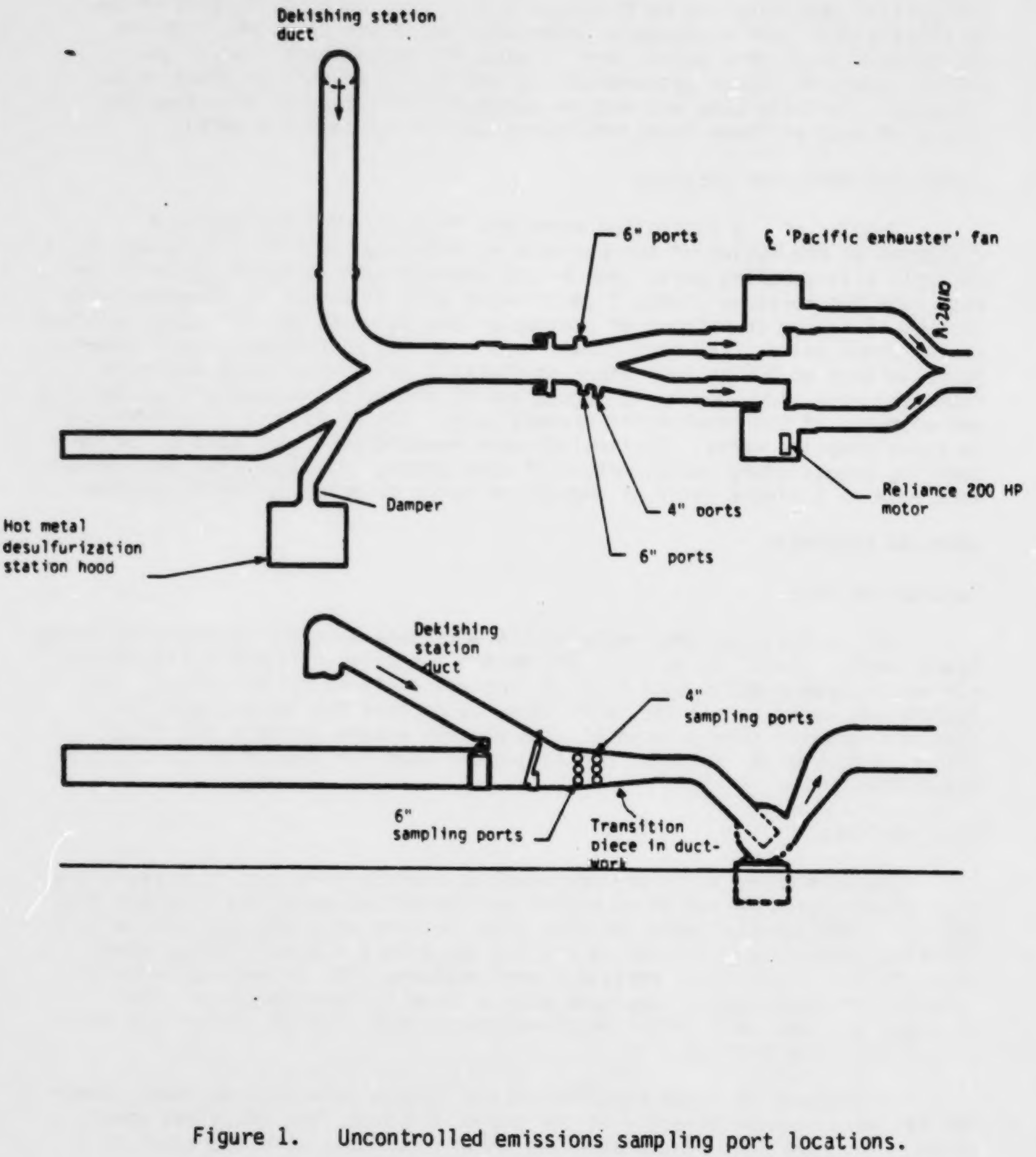

Figure 1. Uncontrolled emissions sampling port locations.

vertical side of the rectangular inlet duct which was 63 inches high and 72 inches wide) were located 24 inches downstream from the beginning and 72 inches upstream from the end of the transition piece in the ductwork. The particulate mass sampling ports (three total, each port equidistant on one vertical side of the rectangular inlet duct which was 57 inches high and 80 inches wide at this point) were located 48 inches downstream of the beginning and 48 inches upstream of the end of the transition piece in the ductwork. Particle size and mass measurements were made at nine sampling points at each of these locations (three points per sampling port).

Controlled Emissions Location

Samples of the controlled emissions from the HMDS process were collected at the outlet of the baghouse as indicated in Figure 2. The particle size sampling ports (one 6-inch diameter port located at 45° to the mass sampling ports on stacks 2 and 5 which were 30 inches in diameter) were located 45 inches downstream of the top of the baghouse and 27 inches upstream of the stack exits. The particulate mass sampling ports (two 4-inch diameter ports located at 90° to each other on stacks 2 and 5 which were 30 inches in diameter) were also located 45 inches and 27 inches downstream of the baghouse and upstream of the stack exits respectively. SO_2 tests were also conducted in these sampling ports. Particulate mass measurements were made at twelve sampling points along two diameters of each stack. Particle size measurements were made at a single point of average velocity as were the SO_2 measurements.

SAMPLING EQUIPMENT

Particulate Mass

All particulate mass measurements were made with the Acurex High Volume Stack Sampler (HVSS) which is an EPA Method 5 sampler. Figure 3 illustrates the heated oven containing a 3 µm cyclone and a 142 mm filter holder. The cyclone was used for all the inlet tests to capture the large, abrasive particles greater than 3 µm in size to prevent damage to the glass fiber filter in the filter holder. No cyclone was used for the outlet tests, just the filter holder.

Particle Size

Two different particle size sampling devices were used to measure the size distribution of the uncontrolled and controlled emissions from the HMDS process. Uncontrolled emission size distributions were measured with a SoRI in-stack, 2-cyclone train (15 µm and 2.5 µm) with a 2.5-inch backup glass fiber filter. Controlled emissions were measured with an Andersen Mark III in-stack cascade impactor equipped with a 15 µm cyclone precutter with straight nozzles. All filter media was Reeve Angel 934 AH. Figures 4 and 5 illustrate these devices.

Since both of these particle sizing devices were used in-stack, these devices were mounted directly on the end of a 5-foot long stainless steel probe. The remainder of the sampling train components were identical to a Method 5 train.

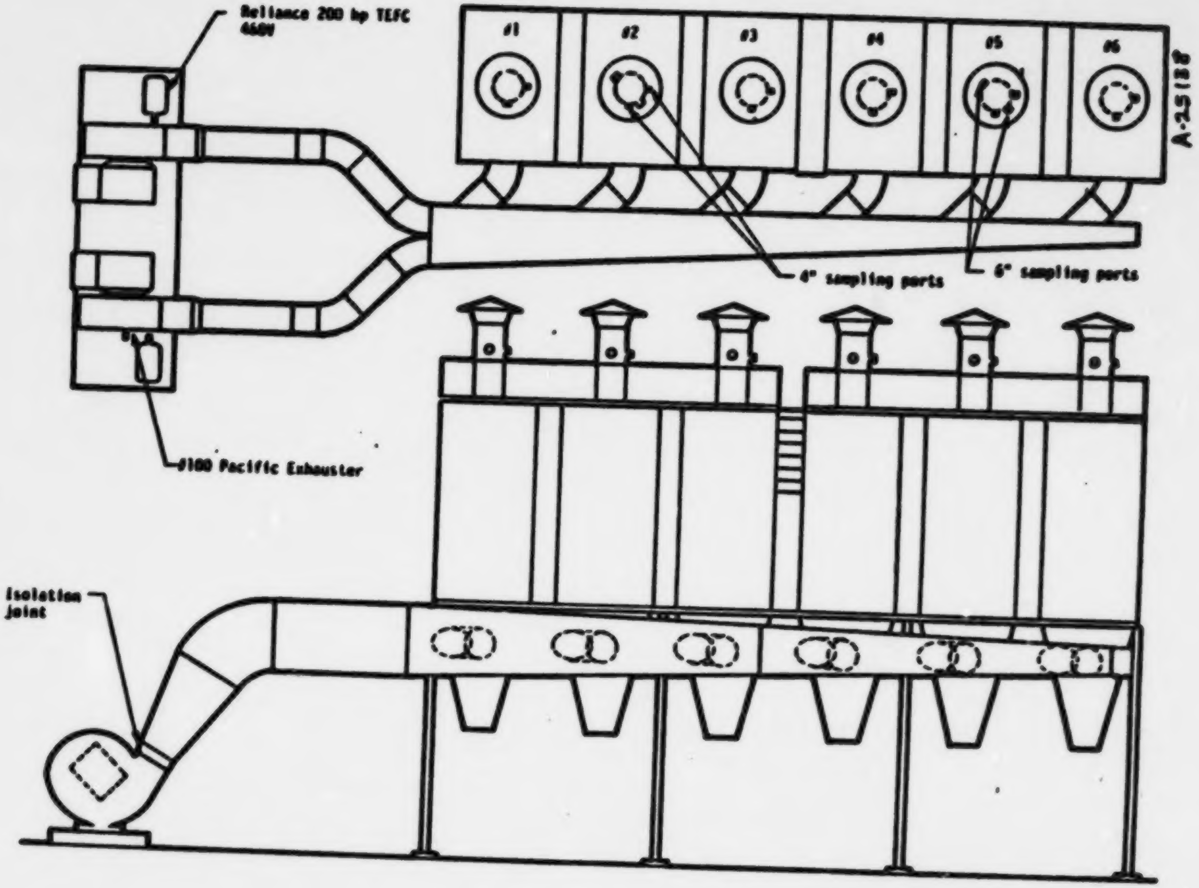

Figure 2. Controlled emissions sampling port locations.

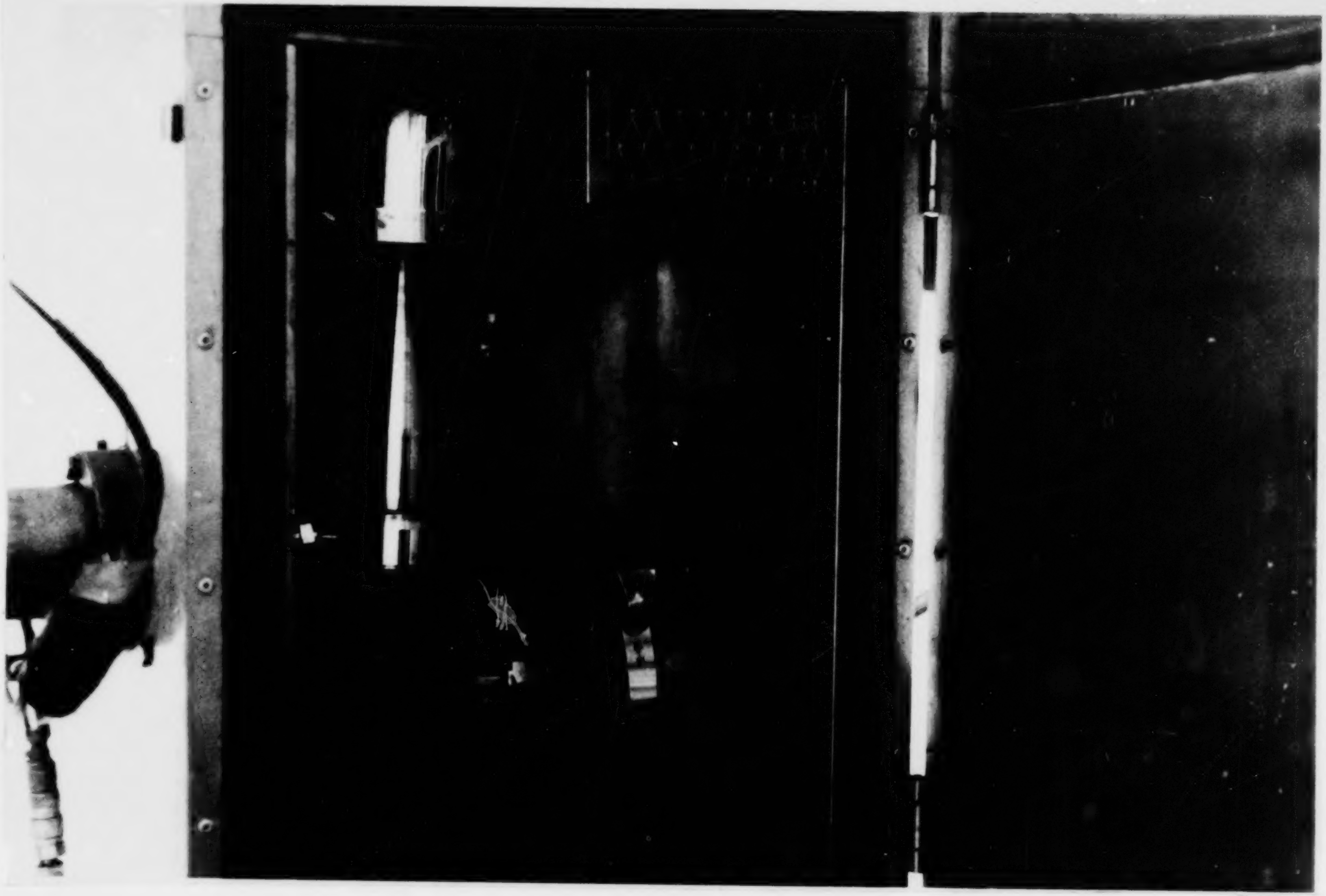

Figure 3. Cyclone and filter holder in heated oven of Method 5 train.

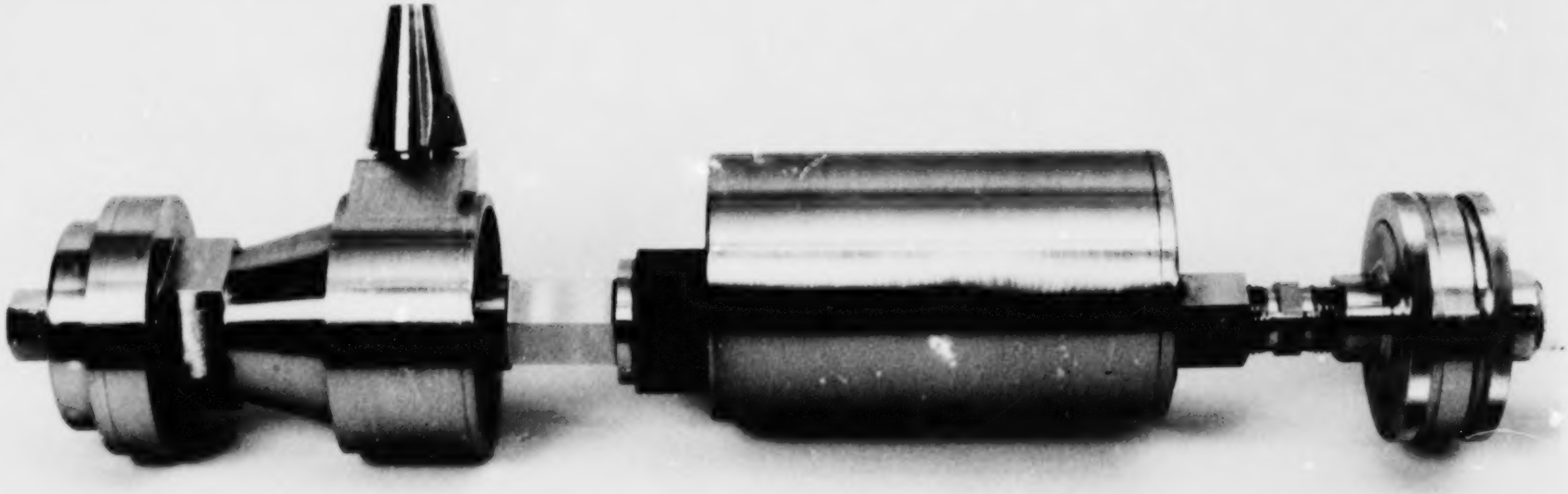

Figure 4. SoRI in-stack 2-cyclone train with 2.5-inch backup filter.

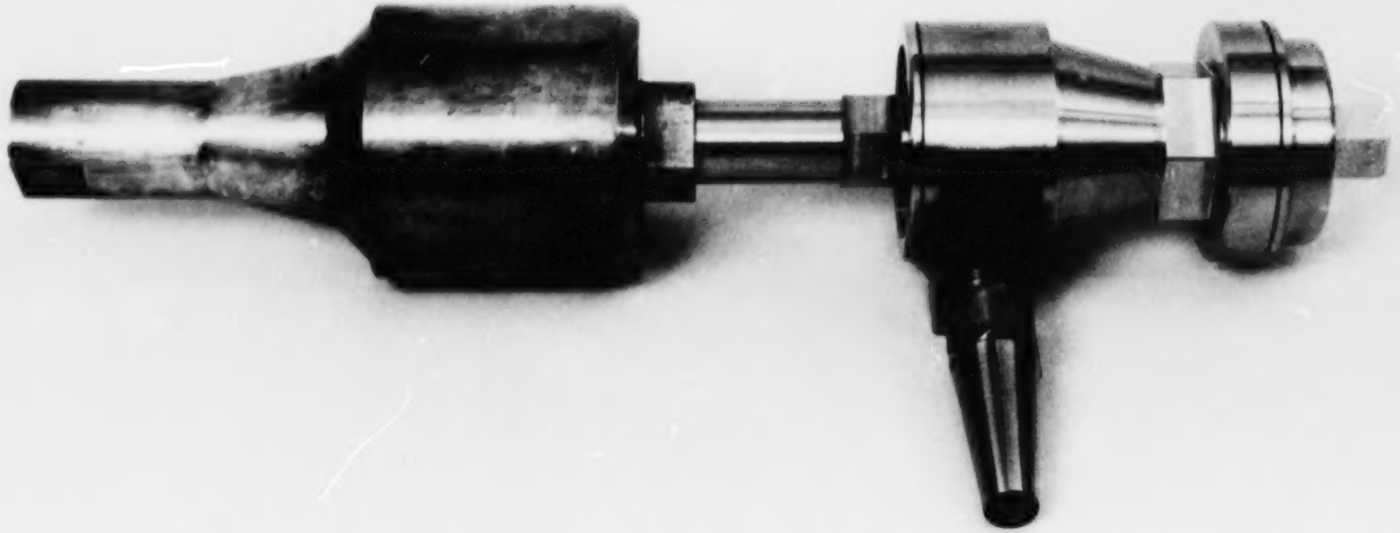

Figure 5. Andersen Mark III cascade impactor with 15 μm cyclone precutter.

Sulfur Dioxide

An EPA Method 8 sampling train was used to sample the controlled HMDS process emissions for SO_2 to maximize the volume of gas sampled since the concentration of SO_2 was expected to be very low.

SAMPLING PROCEDURES

Particle Size Device Comparisons

Since the SoRI 2-cyclone train was a relatively new sampling device, duplicate comparison tests of the SoRI 2-cyclone train and the Andersen Mark III impactor were carried out at the inlet location prior to the test program. Each device was compared against the other to determine if there was any difference in the performance of these devices. For example, the SoRI 2-cyclone train was inserted into one sampling port on one vertical side of the inlet duct while the Andersen Mark III impactor was inserted into the sampling port on the opposite vertical side of the inlet duct. Hence, both devices were in the same measurement plane 6 inches apart (to minimize interference effects of one device on the other but close enough to see the same particle concentration and size distribution). The results of these comparison tests are presented in Table 1 and indicate reasonable agreement between the devices.

The repeatability of each measurement device was also determined in a similar manner. For example, two Andersen Mark III impactors were positioned in the duct work 6 inches apart and were used to simultaneously sample the uncontrolled emissions. The samples were recovered and weighed in an identical manner to determine each device's measurement repeatability. The results of these precision tests are presented in Figures 6 and 7 and indicate good measurement repeatability is possible with careful operation of each device.

Particulate Mass

The particulate mass tests were basically conducted in accordance with EPA Method 5 procedures. Sampling involved careful timing and coordination since particle size and mass determinations were made simultaneously and were dependent on the desulfurization time (varied with the number of torpedo cars to be desulfurized, the degree of desulfurization required, and the start of each torpedo car desulfurization). Since the time of desulfurization varied from 5 to 18 minutes, each sampling point in the inlet duct (nine total) was sampled for 30 seconds for a total sampling time of 4.5 minutes. The volume of gas sampled per test varied from 10 to 15 ft^3. It should be noted that the inlet test location was under considerable negative pressure (upstream of baghouse fan) and the sampling probe was inserted into the duct ~15 seconds before the start of a test with the vacuum pump drawing ~0.05 cfm through the train to prevent the filter paper from lifting off the support screen and possibly tearing and to prevent the impinger liquids from being sucked forward through the train. At the completion of a test, the flowrate through the train was again reduced to ~0.05 cfm as the probe was withdrawn from the duct. The pump was then shut off when the probe was outside the duct.

TABLE 1. COMPARISON TEST RESULTS FOR PARTICLE SIZING DEVICES

Particle Size Device	Volume of Gas Sampled (dscf)	15 µm Less than Stated Size		2.5 µm Less than Stated Size		Total Particulate Mass Concentration (gr/dscf)
		(%)	(gr/dscf)	(%)	(gr/dscf)	
SoRI 2-cyclone train with 2.5 inch backup filter	4.375 4.237	31.7 34.4	0.733 1.120	13.3 12.6	0.308 0.410	2.313 3.256
Andersen Mark III impactor with 15µ cyclone precutter	0.859 0.857	27.1 32.2	0.763 1.090	11.3 14.3	0.318 0.484	2.815 3.385

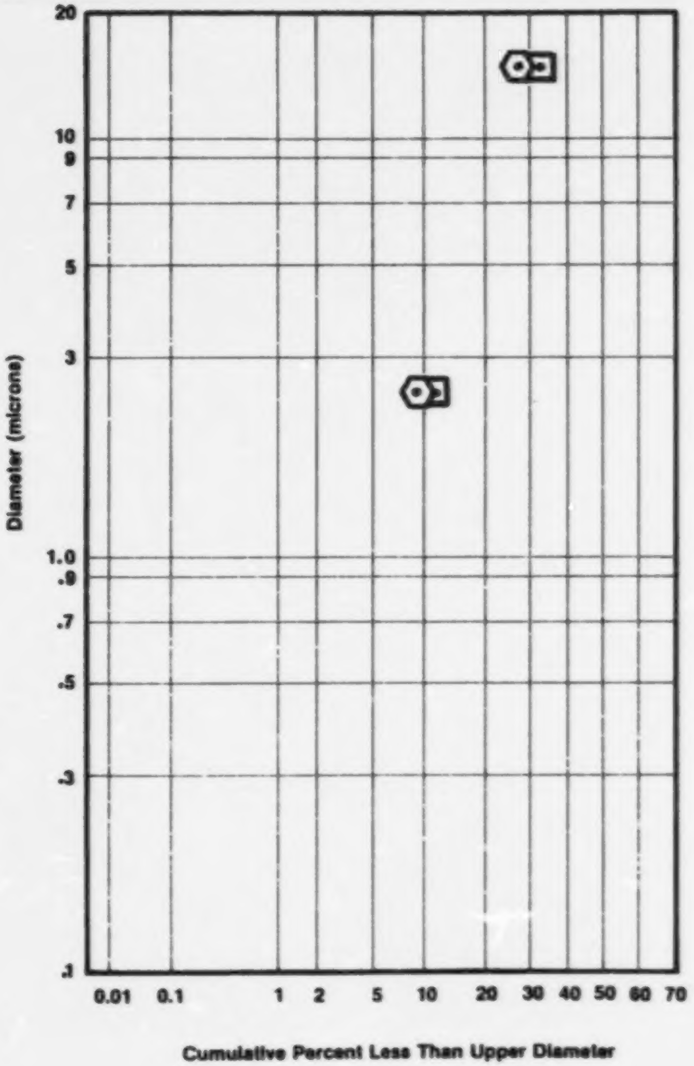

Figure 6. Precision data for SoRI 2-cyclone train.

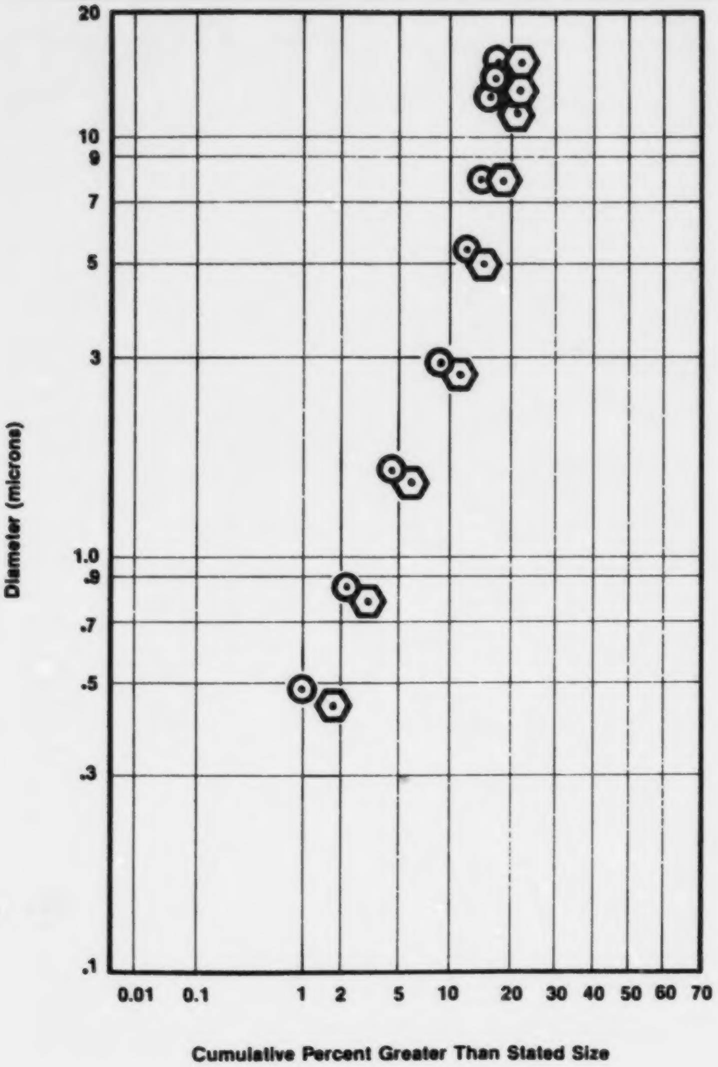

Figure 7. Precision data for Andersen Mark III impactor.

At the outlet test location, several desulfurizations had to be sampled consecutively to collect enough particulate matter for sample evaluation. Hence, each point on two traverses (12 points total) was sampled for 1 minute for a total sampling time of 20 to 24 minutes. The volume of gas sampled per test varied from 47 to 75 ft^3. It took a minimum of two days to complete one test at the baghouse outlet. The outlet test location was at a slight positive pressure and was sampled in a normal manner. Only stacks 2 and 5 were tested simultaneously (for economical reasons) for particulate mass and size.

Particle Size

As a result of the comparison tests, it was shown that the performance of the devices (SoRI 2-cyclone train, Andersen Mark III) were equivalent. Hence, the SoRI 2-cyclone train was used for all inlet tests (high grain loadings) and the Andersen Mark III impactor with a 15 μm cyclone precutter was used for the outlet tests (very low grain loadings).

Prior to conducting a particle size test, each device (SoRI 2-cyclone train and Andersen Mark III impactor) was thoroughly brushed and cleaned with reagent grade acetone. In addition, both the cyclones and the impactor were cleaned in an ultrasonic bath (using a liquid cleanser) after every second or third test.

The sampling procedures for the particle size sampling trains were identical to those of the particulate mass sampling trains except for the number of points sampled during a given desulfurization. Tests conducted with the SoRI device consisted of sampling in one sample port for equal times (2.0 minutes) at each of the three sampling points. Approximately 2.5 ft^3 of gas was sampled per test which provided a more than adequate amount of particulate matter in each collection stage. Three points per test were selected to minimize the number of discrete tests required to traverse the entire duct based on the preliminary velocity measurements which indicated very little horizontal stratification. All three points in all three sample ports were sampled repeatedly to account for particulate stratification (in the vertical direction) over the entire duct. The tests conducted with the Andersen Mark III impactor at the baghouse outlet were done at a single point of average velocity in stacks 2 and 5 since the preliminary measurements indicated very uniform profiles in a given stack although velocities varied from stack to stack. Since the outlet grain loadings were so low (<0.01 gr/dscf), several desulfurizations were tested in order to collect 5 to 6 ft^3 of gas for a weighable sample.

RESULTS

Uncontrolled Emissions

Table 2 summarizes the sampling data obtained with the EPA Method 5 particulate mass train. Table 3 provides a summary of the HMDS production data obtained during these tests. The emission factor data (based on Method 5 measurements) are dependent on the degree of sulfur removal (higher for larger sulfur removal) from the hot metal but does not appear to correlate with the rate of desulfurization; the desulfurization agents injection rate used

TABLE 2. INDIVIDUAL PARTICULATE MASS TEST SAMPLING DATA (Uncontrolled Emissions)

Test Number	Volume of Gas Sampled (dscf)	Particulate Mass (mg)	Particulate Concentration (gr/dscf)	Particulate Emission Rate (lb/hr)
14	14.064	631.54	0.6930	605
18	14.340	2,705.84	2.9919	2,266
19	11.854	2,805.15	3.6519	2,633
20	14.514	696.11	0.7401	605
22	13.314	2,129.50	2.4683	1,862
23	14.154	2,549.61	2.7798	2,151
25	13.960	622.60	0.6882	547
26	12.912	1,028.64	1.2294	904
27	11.710	2,290.14	3.0191	1,977
28	10.908	2,294.71	3.2323	2,017

TABLE 3. HMDS PRODUCTION DATA (Uncontrolled Emissions)

Test No.	Desulfurization Time (min)	Desulfurization Agents		Particulate Mass Emission Rate (lb/min)	Average Desulfurization Rate (tons/min)	Particulate Emission Factor (lb/ton)
		CaC_2 (lb)	$CaCO_3$ (lb)			
14	5.50	333	32	10.08	21.82	0.46
18	9.53 9.97	1063 1033	33 46	37.77	12.31	3.07
19	5.45 5.45 6.93	470 316 613	35 26 51	43.87	20.19	2.17
20	13.55	1043	46	10.08	8.86	1.14
22	10.40 9.03 5.97	814 565 342	42 52 61	31.07	12.87	2.41
23	12.53 13.48 14.02	1006 1095 1191	41 53 113	35.85	9.82	3.65
25	19.00	2073	100	9.07	6.37	1.42
26	8.97	691	58	15.08	11.15	1.35
27	7.35 9.23	551 570	96 64	32.95	14.54	2.27
28	8.75 6.60	558 314	87 40	33.61	15.18	2.21

during these tests was much higher (average 83.3 lb/min) than 50 to 65 lb/min cited by Kaiser and the CaC_2 usage averaged 6.4 lb/ton hot metal to obtain an average sulfur reduction of 65.2 percent compared to the cited 3.6 lb CaC_2/ton hot metal for 60 percent sulfur removal.

Controlled Emissions

Table 4 summarize the sampling data obtained with the EPA Method 5 particulate mass train. Table 5 provides a summary of the HMDS production data obtained during these tests. The emission factor data (based on Method 5 measurements) are dependent on the degree of sulfur removal (higher for larger sulfur removal) from the hot metal; the average desulfurization injection rate was 83.9 lb/min and the CaC_2 usage averaged 3.95 lb/ton hot metal to obtain an average sulfur removal of 50 percent.

SUMMARY OF TEST RESULTS

Emission Factor Data

The average emission factor (based on Method 5 measurements) for uncontrolled HMDS process emissions was 1.09 ±0.44 lb/ton for one torpedo car (TC), 2.53 ±0.47 lb/ton for two TC's, and 2.74 ±0.79 lb/ton for three TC's. Based on the particle size measurements made with the SoRI 2-cyclone train, approximately 25 percent of these particles are less than 15 μm in size and 12 percent are less than 2.5 μm in size.

The average emission factor (based on Method 5 measurements for controlled HMDS process emissions was 0.009 ±0.003 lb/ton. Based on the Andersen impactor measurements, the D_{p50} for these emissions was 3.4 μm.

The average mass removal efficiency of the baghouse based on Method 5 measurements (not simultaneous) was 99.36 percent and no SO_2 was detected in the baghouse exhaust.

Comparison of Sampling Train Data

Tables 6, 7, 8 and 9 compare the Method 5 train test results with those obtained by the particle size trains. All inlet particulate mass tests traversed the entire inlet duct; all particle size tests were done at three points only as follows: tests 18, 19, and 26 were done in the top sampling port (points 1, 2, 3); tests 20, 23, and 25 were done in the middle sampling port (points 4, 5, 6); tests 22, 27, and 28 were done in the bottom sampling port (points 7, 8, 9); Method 5 train (front half only) concentrations were 21 percent greater than the SoRI train concentrations for the top port, 8 percent greater for the middle port, and 23 less for the bottom port; there is obviously particulate stratification from top to bottom in the inlet duct.

All outlet particulate mass tests traversed both baghouse stacks; all particle size tests were done at a single point of average velocity; in all but one case, the Method 5 particulate mass concentrations were

TABLE 4. INDIVIDUAL PARTICULATE MASS TEST SAMPLING DATA (Controlled Emissions)

Test Number	Volume of Gas Sampled (dscf)	Particulate Mass (mg)	Particulate Concentration (gr/dscf)	Particulate Emission Rate (lb/hr)
15	65.909 75.296	31.09 104.54	0.0073 0.0214	0.96 2.65
16	47.718 51.900	33.71 71.75	0.0109 0.0213	1.31 2.70
17	57.159 57.355	17.84 60.20	0.0048 0.0162	0.63 2.17

TABLE 5. HMDS PRODUCTION DATA (Controlled Emissions)

Test No.	Desulfurization Time (min)	Desulfurization Agents		Particulate[a] Mass Emission Rate (lb/min)	Average Desulfurization Rate (tons/min)	Particulate Emission Factor (lb/ton)
		CaC_2 (lb)	$CaCO_3$ (lb)			
15	6.30	475	34	0.180	17.60	0.010
	4.48	263	28			
	6.40	409	75			
	6.37	413	36			
	6.32	426	35			
	7.02	464	51			
	7.42	628	35			
	6.97	568	49			
	6.97	595	59			
16	8.48	929	34	0.202	18.31	0.011
	7.77	736	47			
	8.13	774	62			
	3.77	296	33			
	6.22	475	44			
	4.83	356	31			
	5.93	537	34			
	6.73	562	47			
	7.13	540	63			
17	4.72	391	32	0.132	29.01	0.005
	4.13	216	26			
	4.12	268	60			
	3.83	300	33			
	3.73	266	33			
	4.12	254	30			

[a] Computed using average Method 5 concentration for two stacks and average volumetric flowrate from inlet tests

TABLE 6. COMPARISON OF METHOD 5 AND SoRI TRAIN DATA (Top Port)

Sampling Device	Sampling Location (Inlet Duct)	Volume of Gas Sampled (dscf)	Particulate Mass Concentration (gr/dscf)
Acurex Method 5 high volume stack sampler	All 9 points	14.340 11.854 12.912	2.9119 3.6519 1.2294
SoRI 2-cyclone train with 2.5 inch backup filter	Points 1,2,3	2.550 2.694 2.785	2.3575 2.8104 0.9740

TABLE 7. COMPARISON OF METHOD 5 AND SoRI TRAIN DATA (Middle Port)

Sampling Device	Sampling Location (Inlet Duct)	Volume of Gas Sampled (dscf)	Particulate Mass Concentration (gr/dscf)
Acurex Method 5 high volume stack sampler	All 9 points	14.514 14.154 13.960	0.7401 2.7798 0.6882
SoRI 2-cyclone train with 2.5 inch backup filter	Points 4,5,6	2.679 2.651 2.749	0.4496 2.6186 0.8102

TABLE 8. COMPARISON OF METHOD 5 AND SoRI TRAIN DATA (Bottom Port)

Sampling Device	Sampling Location (Inlet Duct)	Volume of Gas Sampled (dscf)	Particulate Mass Concentration (gr/dscf)
Acurex Method 5 high volume stack sampler	All 9 points	13.314 11.710 10.908	2.4683 3.0181 3.2323
SoRI 2-cyclone train with 2.5 inch backup filter	Points 7,8,9	2.644 2.742 2.722	2.8942 2.9927 5.3917

TABLE 9. COMPARISON OF METHOD 5 AND ANDERSEN MARK III IMPACTOR DATA (Stacks 2 and 5)

Sampling Device	Sampling Location (Outlet Stacks)	Volume of Gas Sampled (dscf)	Particulate Mass Concentration (gr/dscf)
Acurex Method 5 high volume stack sampler	All 12 points	65.909 75.296 47.718 51.900 57.159 57.355	0.0073 0.0214 0.0109 0.0213 0.0048 0.0162
Andersen Mark III impactor with 15 μm cyclone precutter	Average point	5.868 6.030 6.265 5.435 6.249 5.983	0.0078 0.0060 0.0054 0.0084 0.0044 0.0066

considerably greater (average 50 percent) than corresponding impactor concentrations: the volumetric flowrates through stacks 2 and 5 showed very little difference, but the mass concentrations were significantly different (stack 5 always greater than 2).

DEMONSTRATION OF THE USE OF CHARGED FOG IN CONTROLLING FUGITIVE DUST FROM LARGE-SCALE INDUSTRIAL SOURCES

by

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ABSTRACT

A unique device for the control of particulate emissions works on the principle that most industrial pollutants acquire an electrostatic charge as they are dispersed into the air. If this charged airborne material is exposed to an oppositely charged water fog, the charges act to enhance the contact between the particulates and the fog droplets, resulting in rapid agglomeration and particle fallout. A device that generates charged fog has now been substantially developed and is being offered commercially by The Ritten Corporation.

TRC-Environmental Consultants, Inc. has been contracted by EPA/IERL/RTP to test the Ritten Corporation's Fogger IV on several large-scale fugitive dust sources. This paper discusses the initial test at a sand and gravel operation and presents preliminary test results in terms of percent reduction in TSP. The changes in fogger effectiveness due to variations in operational parameters are discussed. The initial tests indicate overall fogger efficiencies of approximately 70 percent.

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DEMONSTRATION OF THE USE OF CHARGED FOG
IN CONTROLLING FUGITIVE DUST
FROM LARGE-SCALE INDUSTRIAL SOURCES

INTRODUCTION

A spray of fine water droplets is a well-known means of airborne dust removal. Various types of scrubbers rely on water droplets to sweep particles from the inlet gasses and water sprays are often used in mining and material handling for dust suppression. Unfortunately, water sprays are not very efficient in removing dust from the ambient air.

One means of improving the efficiency of water sprays is by applying a charge to the spray that is opposite in polarity to the charge of the dust to be suppressed. It has been found that most industrial pollutants and naturally occurring fugitive dusts acquire an electrostatic charge as they are dispersed into the air. If this charged, airborne material is exposed to an oppositely charged water spray there is enhanced contact between the particulates and the water droplets. After contact is made, the wetted particulates agglomerate rapidly and fall out of the atmosphere.

The charged sprays can be further improved by atomizing the water droplets so that a fog is produced. The fineness of the particles enhances the charge carrying capabilities in the spray. Furthermore, Hoenig (1977)[1] has demonstrated that the greatest effectiveness is obtained when the water droplets are of a similar size to the dust particles to be controlled. Lastly, less water is required when fog is used, thus reducing operating costs.

A device capable of producing this fine spray and applying a charge to it is known as a charged fogger. A charged fogger uses a nozzle to produce the fog, an induction ring to charge the fog as it leaves the nozzle, and a fan to transport the fog to the dust source. The operation of the fogger requires a water supply, a pressurized air supply, and power. There are several such devices on the market, tailored to the size and type of industrial application.

The charged fogger is intended primarily for fugitive dust sources that cannot reasonably be controlled via conventional means such as hooding. Such sources include materials handling operations (transfer points and conveyors), truck and railroad car loading and unloading, front end loaders, ship loading, grain silos, and mining operations. The charged fog concept has been applied to operations as small as a hand grinder and as large as a quarry.

Although the charged fog concept has been widely applied to industrial souces of fugitive dust, little data is available regarding fogger control efficiency. To obtain such data, the Industrial Environmental Research Laboratory of the Environmental Protection Agency at Research Triangle Park, North Carolina, (IERL/EPA/RTP) contracted TRC-Environmental Consultants, Inc. (TRC) to conduct a full scale demonstration of a charged fogger on several appropriate industrial fugitive emission sources. In particular, IERL/EPA was interested in testing the largest fogger, designated "Fogger IV", manufactured by the Ritten Corporation of Ardmore, Pennsylvania, on several sources within the iron and steel and sand and gravel industries.

The sources considered for testing included materials transfer, conveying, grinding, crushing, and truck and railroad car loading and unloading. The requirements for a test site included isolability from other dust sources, availability of necessary utilities, relative difficulty of control by other methods, representativeness to the general industry, relatively continuous operation, and fairly heavy dust production to facilitate sampling.

Following numerous visits to iron and steel and sand and gravel sites, several suitable sources were selected for field testing the charged fogger. The source chosen for the first test was the primary rock crusher operation at a sand and gravel site in Connecticut.

DESCRIPTIONS OF SITE AND TEST EQUIPMENT

Figure 1 is a plot plan of the primary crusher operation showing the locations and dimensions of the various structures. Descriptions of the site and test equipment are given in the following subsections.

Test Site

The inital fogger test site was a primary rock crusher. Approximately 100 dump trucks per day, each carrying loads of approximately 45 Mg (50 tons) of quarry rock (basically basalt) mixed with dirt, back up to the crushing pit to unload. Unloading times vary from 30-60 seconds, depending on conditions in the pit. The pit itself is roughly 8 meters long and 6 meters wide. The crushing is done by a Superior 4265 gyrotory rock crusher. There is a two story computer control building to the north side of the crushing pit, a control shed to the east, and a large paved area to the south side. All approach roads and areas around the buildings and pit are paved and kept reasonably clean through frequent sweepings and waterings.

Fugitive dust emissions result from the dumping and crushing operations. The truck unloading is the primary source of dust with the major portion coming from dust boil-up at the rear of the pit. There is also dust at the rear of the truck during the dump. The crushing procedure itself also produces dust, but to a much lesser degree than the unloading process.

Charged Foggers

Two identical foggers were specially designed for TRC and EPA by the Ritten Corporation of Ardmore, Pennsylvania. Ritten's standard Fogger III was modified and upgraded in order to allow for variations of parameters. The final configuration, designated "Fogger IV", is shown schematically in Figure 2.

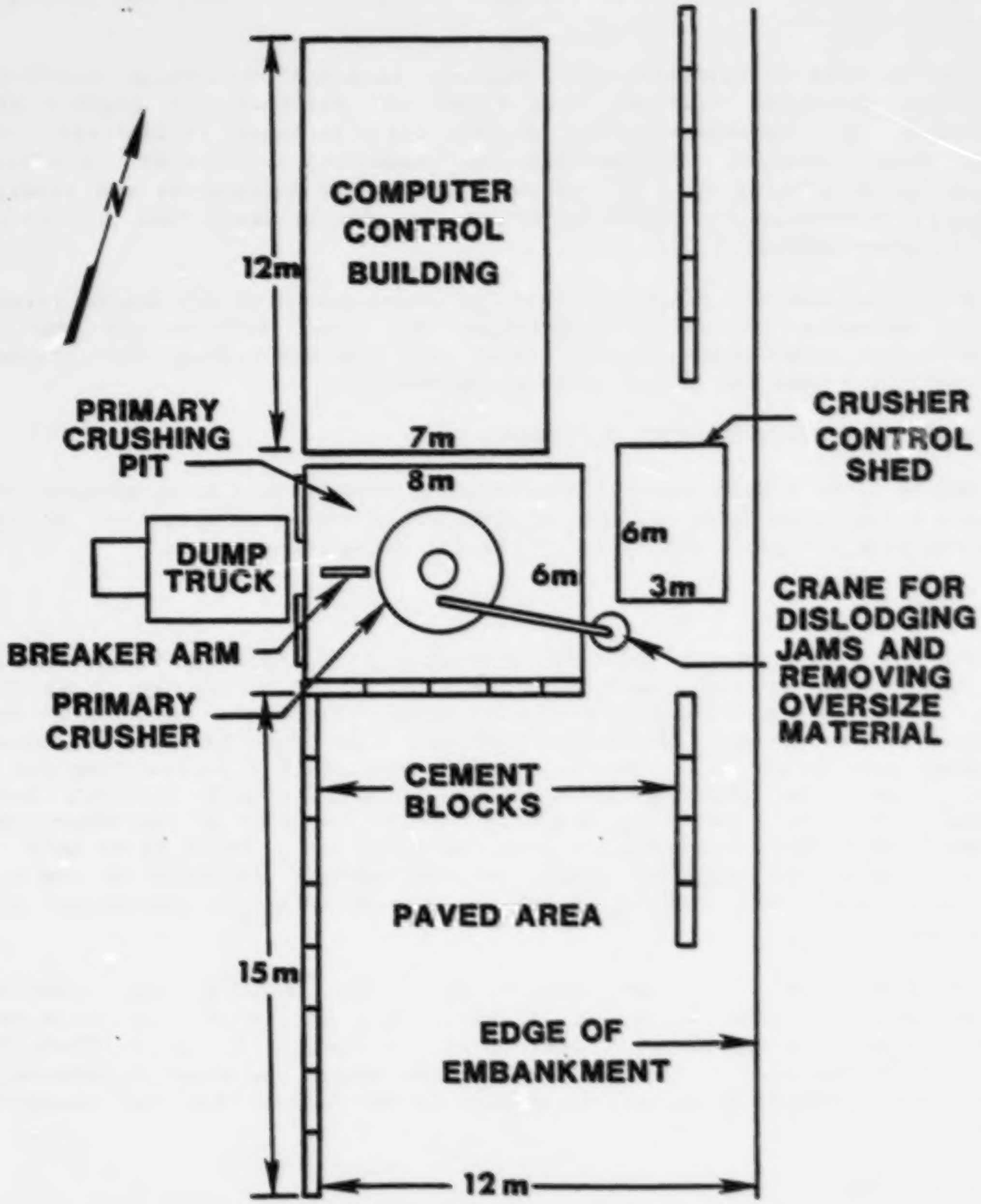

Figure 1. Primary crusher plot plan.

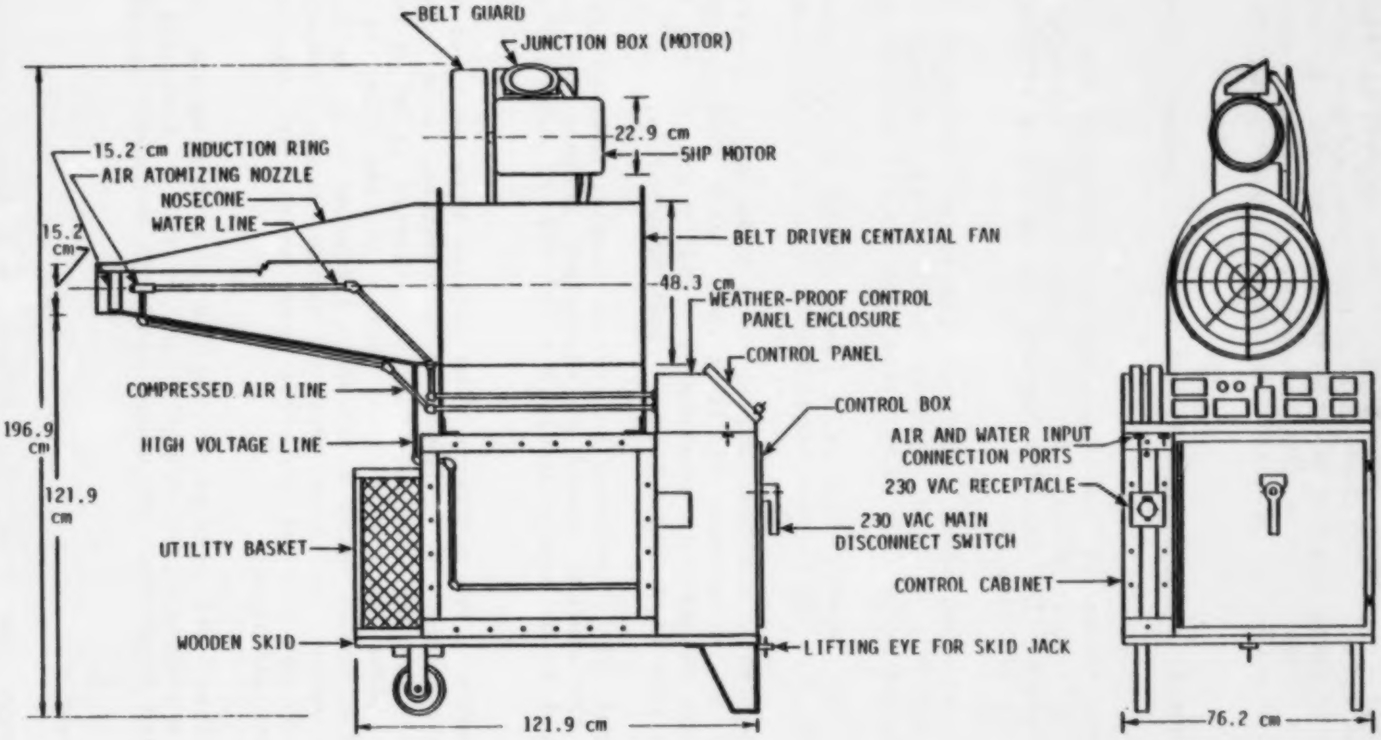

Figure 2. Schematic of the Ritten Corporation's Fogger IV.

In the generation of the charged fog by the Fogger IV, water is atomized via a compressed air supply and ejected from a nozzle. As the fog leaves the nozzle, it passes through an induction ring where either a positive or negative charge, depending on the nature of the dust, is applied to the spray. A flow of air around the nozzle, provided by a centaxial fan, projects the fog towards the dust source. A control panel, located on the back of the fogger, allows for fogger operation and parameter variability. A schematic of the control panel is shown in Figure 3.

The requirements for and capabilities of the operational parameters are as follows:

- Air supply to nozzle - A compressed air supply of 5.6 - 8.8 kg/cm^2 (80-125 PSI) is required. For the tests the air was supplied by a 2 hp compressor. The air flow through the nozzle is variable from 0 - 11.3 m^3/hr (0-400 SCFH).
- Water flow - The water supply to the fogger should be around 3.5 kg/cm^2 (50 PSI) which is typical "shop" water pressure. The water flow through the nozzle is variable from 0 - 151 l/hr (0-40 GPH).
- Power - The foggers require a power supply of 230 volts, single phase, 60 Hz. The current requirements do not exceed 35 amps.
- Centaxial fan - The fan, driven by a 5 hp explosion-proof motor, operates at a maximum of 79 m^3/min (2800 SCFM). The maximum output air velocity is approximately 3048 m/min (10,000 FPM). The fan flow rate is variable from 0 - 100% of capacity.
- Charge per drop - Assuming an average droplet size of approximately 60 µm, the average number of elementary charges per droplet was calculated to be approximately 8×10^4 for 75 l/hr (20 GPH) water flow.
- Flow spectra - Two different flow nozzles were used for the tests, both manufactured by Delavan in Des Moines, Iowa. One nozzle produced a conical spray of droplets estimated to be in the 50 - 70 µm size range while the other had a heavier flow capacity and produced a conical spray of droplets estimated to be in the 60 - 80 µm size range. A third type of nozzle, which produces a flat spray, was not yet available for these tests, but will be used at subsequent locations.

The two foggers were tested at various locations around the pit to determine the arrangement for optimum dust control. Placement was also dependent on wind direction. The exact positions are described in the next section.

Sampling Equipment

The equipment used for particulate measurements included seven hi-volume samplers and a wind recording system. The hi-vols were manufactured by Misco Scientific and had automatic flow control. This

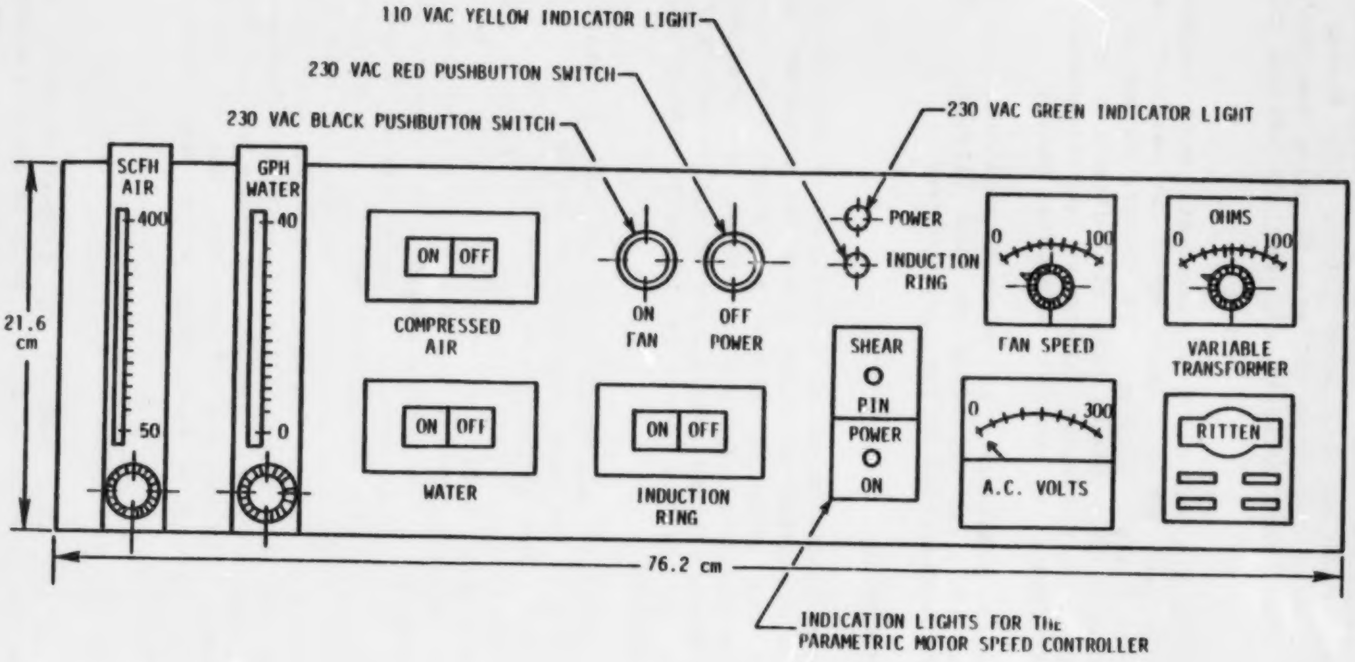

Figure 3. Schematic of the Fogger IV control panel.

enabled the mass flow rate to be held constant irrespective of filter loading, atmospheric conditions, and line voltage changes. Two of the hi-vols were fitted with Anderson Model 7000 Size Selective Inlets (SSI's) which are designed to remove all particulates larger than 15 μm from the sampled air before filtering the remaining particulates onto a standard hi-vol filter. Two other hi-vols were fitted with Sierra Instruments Series 230 4-stage cascade impactors (CI's). By using the SSI's and CI's, the charged fogger efficiency could be examined for various particle size ranges.

The wind velocity and direction measurements were recorded using a Climatronic Mark III Wind system. Wind speed is measured with a 3-cup anemometer coupled to a light chopper. The chopper output is converted to DC voltage and recorded on a chart. The wind direction is measured by a wind vane coupled to a precision low-torque potentiometer. The wiper voltage of the potentiometer is recorded on another chart.

The hi-vols were positioned at various locations and in various combinations around the pit, depending on wind direction. The sampling array for each test is described in the next section.

TEST PROGRAM AND PROCEDURE

The test program consisted of 32 runs during 6 days of testing. The test conditions are presented in Table 1 and the equipment positions for each set of runs are shown in Figure 4. Conditions at the crusher prevented extensive parameter variations. Water was provided by a tank with a small pump which limited nozzle flow to approximately 80 l/hr. Fan speed was reduced to 80% of capacity to help reduce excessive dust reentrainment in the pit.

The sampling procedure was essentially the same for each test. Upon arrival at the test site the wind recording system was set up and the wind direction determined. The hi-volume samplers were then positioned in a sampling array downwind of the crushing pit. The foggers were positioned to control the dust cloud while not spraying directly into the samplers. Once the equipment was positioned, the pre-weighed hi-volume filters were placed into the samplers. The samplers were then turned on simultaneously just prior to the first truck dump of a predetermined sequence of trucks (typically 8 trucks provided sufficient material for sampling purposes). For the runs with the foggers in operation, the foggers were also turned on at this time and adjusted to the predetermined fogger operational parameter conditions. After the last truck of the sequence had dumped into the pit and crushing was completed, the samplers and foggers were all stopped and the filters removed. At the end of the day, all of the filters were returned to TRC's chemistry laboratory where they were subsequently desiccated and weighed.

PRELIMINARY RESULTS AND DISCUSSION

The majority of the test runs at the primary crusher, numbers 7-31, were completed before the final filter weights were available from the chemistry laboratory. Upon examining the data, several important factors came to light. In almost all cases, the TSP levels, as measured by the various samplers, showed increases above the uncontrolled levels when

Table 1. TEST CONDITIONS - PRIMARY CRUSHER

Run Designation No.	Equipment Positions	Date	Time	Ambient Temp. (°C)	Relative Humidity (%)	Wind Direction	Wind Speed (m/sec)	No. of Trucks	Fogger 803018 Water Flow (l/hr)	Fogger 803018 Air Flow (m^3/hr)	Fogger 803018 Fan Speed (%)	Fogger 803018 Sign of Charge	Fogger 803018 Nozzle* Type	Fogger 803019 Water Flow (l/hr)	Fogger 803019 Air Flow (m^3/hr)	Fogger 803019 Fan Speed (%)	Fogger 803019 Sign of Charge	Fogger 803019 Nozzle* Type
7	Fig. 4a	10-13-80	0938-1000	9	77	N-E	2-5	8										
8	↓	↓	1050-1129	10	77	NNW	↓	8	61	4.2	80	(0)	1	68	4.2	80	(0)	1
9	↓	↓	1300-1381	13	70	↓	↓	8										
10	↓	↓	1326-1350	13	70	↓	↓	8	68	4.2	80	(-)	1	68	4.2	80	(-)	1
11	↓	↓	1355-1434	13	70	↓	↓	8	72	4.0	80	(+)	1	68	4.0	80	(+)	1
12	Fig. 4b	10-14-80	0833-0915	6	72	WNW	Var. w/gusts to 9	8										
13	↓	↓	0933-1005	6	72	↓		8	60	2.3	80	(0)	1	68	2.3	80	(0)	1
14	↓	↓	1022-1050	7	72	↓		8	57	2.3	80	(+)	1	72	1.6	80	(+)	1
15	↓	↓	1059-1125	7	72	↓	↓	8	53	2.7	80	(-)	1	64	1.8	80	(-)	1
16	↓	↓	1245-1305	9	72	↓	↓	8	53	2.4	80	(-)	1	61	1.4	80	(-)	1
17	↓	↓	1313-1346	10	72	↓	↓	8										
18	Fig. 4c	10-15-80	0949-1026	9	36	Calm	Calm	10										
19	↓	↓	1039-1113	9	36	↓	↓	10	68	4.0	50	(-)	2	66	4.0	50	(-)	2
20	↓	↓	1116-1156	11	36	↓	↓	8	76	4.1	50	(0)	2	76	3.6	50	(0)	2
22	Fig. 4d	10-16-80	0940-1003	12	57	Calm	Calm	8										
23	↓	↓	1021-1038	12	57	↓	↓	4	76	2.8	80	(+)	2	76	4.4	80	(+)	2
24	↓	↓	1056-1127	16	57	↓	↓	8	72	2.0	80	(-)	2	76	2.6	80	(-)	2
25	↓	↓	1251-1314	20	52	SSW	2-5	8	72	2.6	80	(+)	2	72	3.1	80	(+)	2
26	↓	↓	1323-1345	20	52	↓	↓	8	77	2.7	80	(0)	2	77	2.8	80	(0)	2
27	↓	↓	1350-1412	20	52	↓	↓	8										
28	Fig. 4e	10-17-80	0850-0927	21	55	Calm	Calm	8										
29	↓	↓	0936-0927	21	55	↓	↓	8	76	3.4	70	(0)	2	76	4.0	70	(0)	2
30	↓	↓	1016-1045	21	55	↓	↓	8	80	2.2	70	(+)	2	80	2.8	70	(+)	2
31	↓	↓	1105-1135	21	55	↓	↓	8	76	3.6	70	(-)	2	76	2.8	70	(-)	2
32	Fig. 4f	10-24-80	925- 943	4	82	Calm	Calm	6			80					80		
33	↓	↓	950-1004	4	82	↓	↓	6	76	4.2	80	(0)	2	74	4.2	80	(0)	2
34	↓	↓	1010-1025	5	82	N-E	↓	6			80					80		
35	↓	↓	1027-1040	5	82	↓	↓	6	76	4.7	80	(0)	2	76	4.4	80	(0)	2
36	↓	↓	1045-1112	5	82	↓	↓	6	74	4.8	80	(-)	2	78	4.1	80	(+)	2
37	↓	↓	1120-1130	6	82	↓	↓	6			80					80		
38	↓	↓	1244-1325	11	68	SE-S	1-2	10			80					80		
39	↓	↓	1334-1403	11	68	SE-S	1-2	10	78	4.2	80	(0)	2	78	4.2	80	(0)	2

* Type 1: low flow
Type 2: heavy flow

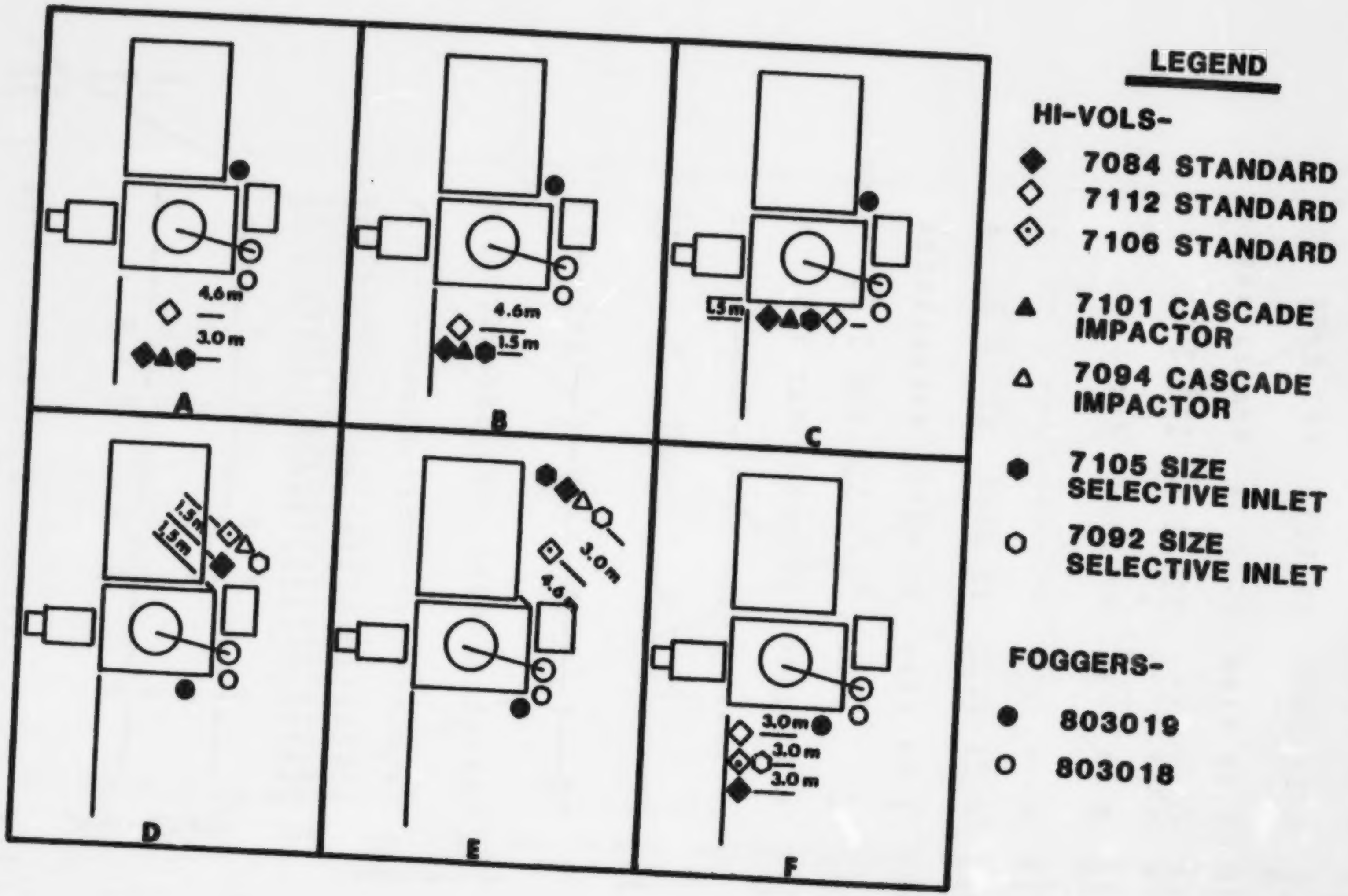

Figure 4. Test equipment positions.

uncharged fog was applied to the crushing operation. Although this result was unexpected, further analysis soon found the problem. The fans in the foggers which create the airflow that projects the fog toward the dust source are so powerful that they were actually creating an artificial wind effect. The uncontrolled dust plume was only subject to the ambient wind whereas the controlled plume was being radically "directed" by the fogger air jets. This discovery produced the need for a final series of tests wherein the uncontrolled baseline TSP levels were recorded with the fans on with no water added.

Another concern that developed was with the intermittent nature of the truck dumps. In some cases, eight trucks would unload within twenty minutes while at other times it would take thirty or forty minutes. The data was therefore reduced on a per-truck basis since the unloading and crushing times, the times when the vast majority of the dust is produced, were essentially the same for all dumps. The data were also slightly adjusted to account for deviations of the actual sampler flow rates from the design flow of 1.1 m^3/min (40 cfm).

While the data from runs 7-31 did not reveal information regarding overall fogger efficiency, it did provide insight into the increase in efficiency due to charging the fog versus uncharged fog. This efficiency could be further examined with regards to particle size, distance from the pit, and positive charge versus negative charge. Not all of the runs produced usable data since the fog impinged on the samplers during some tests.

The data from runs 32-39 were used to determine fogger efficiency with respect to uncharged fog. The spacing of the samplers also allowed for the examination of efficiency versus distance from the pit. This information was then combined with the data from runs 7-31 to calculate overall fogger efficiency.

Attempts were made at obtaining information on visibility improvement via EPA Method 9 (visual determination of opacity). It was found that the opacity of the fog was similar to the opacity of the uncontrolled dust plume so that no real visibility improvement was noted.

Figure 5 presents the preliminary test results from the initial charged fogger tests at the primary crusher site. The left side of the figure shows the percent reduction in TSP levels when an uncharged water fog was used to control the fugitive dust. The right side of the figure shows the additional percent reduction in TSP levels when a charge was applied to the fog. The data from this figure reveal several important results, as discussed in the following subsections.

Uncharged Fog Efficiency

Based on the limited amount of data for fan only versus uncharged fog, it appears that a water spray alone is approximately 30-40% efficient in reducing the fugitive dust levels from the primary crusher. It also appears that this efficiency is independent of particle size and the distance from the pit.

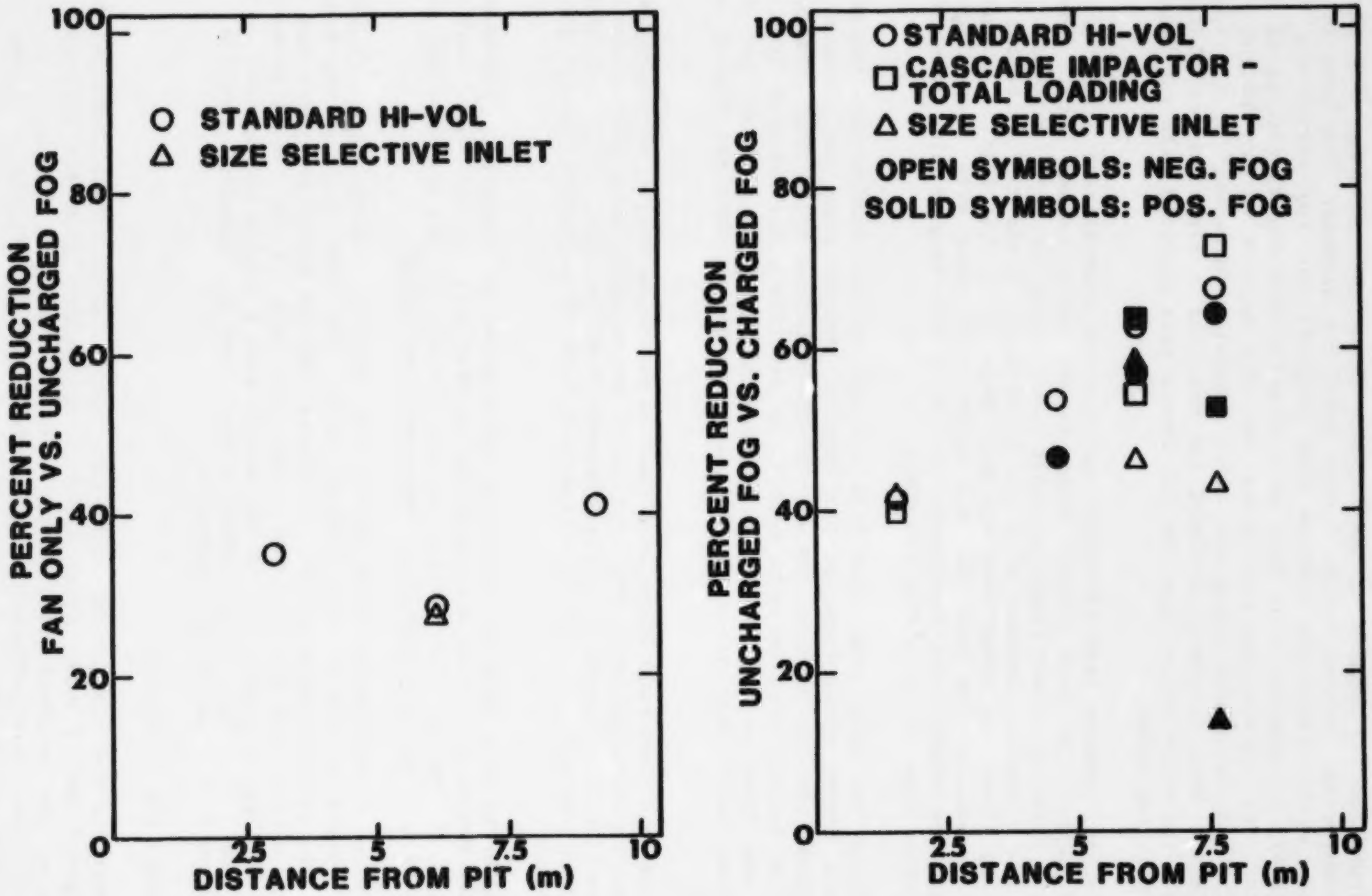

Figure 5. Percent reduction in TSP levels due to fogging of primary crusher.

Efficiency Increase Due to Charging of Fog

By applying a charge to the water spray, the fugitive dust levels were reduced 40-70% over the levels recorded using uncharged fog. There appears to be a trend of increasing reduction with increasing distance from the pit. This apparent phenomenon is not explainable at this time, but it may have something to do with agglomeration and particle fallout. This possible distance factor will be examined further in future tests.

Figure 5 also shows that TSP reduction due to charging is essentially the same regardless of whether a positive or a negative charge is applied to the spray. This indicates that the dust cloud contains a mixture of particles, some with negative charge and some with positive charge. This is consistent with the findings of other researchers, namely Hoenig (1977)[1] and Kunkel (1950)[2].

TSP reduction appears to be the same for the respirable size range ($\leq$ 15μm), as measured with the hi-vols with size selective inlets, as for the size range sampled with the standard hi-vol ($\leq$ 30μm). It was hoped that the use of the cascade impactors would provide additional information on efficiency versus particle size, but the results proved unusable. Almost all of the material collected by the hi-vols fitted with the impactors was collected on the back-up filter. This indicates that there was severe particle bounce between the impactor stages. Perhaps tests at sources with finer dust will yield more useful information.

Overall Fogger Efficiency

By combining the results presented in Figure 5, it is possible to calculate an overall collection efficiency for the charged foggers. Based on the preliminary data, the use of charged fog can reduce the fugitive dust levels that result from the primary rock crushing operation approximately 65-75%. It is felt that this reduction could be even greater through the use of additional foggers, wind baffles to reduce turbulence, and increased water flow.

FUTURE WORK

The two foggers are currently being tested at the second source which is a secondary rock crusher at another site in Connecticut. At this site, fugitive dust results from the fall of the crushed material onto a conveyor belt. This dust is released to the atmosphere through openings at the base of the operation. The foggers have been positioned so as to blanket this area with a cloud of charged fog. Testing should be completed at this location by the end of November.

Following the tests at the secondary crusher, the next sources to be tested will be within the iron and steel industry. Negotiations are currently underway for testing at two different steel companies - one in the eastern United States and one in Canada. At the one steel company, there are two possible sources for testing the foggers. One source is a sinter plant pug mill which mixes water with baghouse dust for dust suppression before recycling the material back through the plant. Even with the water addition there is a significant amount of fugitive dust around the source. The second source is the hot fume that results in a cast house from the filling of a ladle car with molten iron from a cast. At the other steel company, a possible source for testing is a coke screening operation. Coke is transferred from a conveyor belt onto a shaker screen where it is sorted by size. The shaking results in copious amounts of dust. There is also the possibility of testing some limestone handling operations, such as transfer points and truck unloading, at this location.

The steel company tests mentioned above will most likely be performed in the winter and early spring. Following completion of all field tests, a final report will be prepared for the EPA presenting the results.

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A GRAVEL BED FILTER WITH FLUIDIZED-BED DURING REVERSE CLEANING

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ABSTRACT

In order to meet the needs for cleaning large quantity of high temperature fume from iron and steel plants, Safety Technology Research Institute of Metallurgical Industry Ministry of China has developed a new type of gravel bed filter in which the gravel bed fluidizes during reverse cleaning. Being designed on the principle of bulb forming and fluidization, this kind of filter can clean dust remained in the filtrating bed by fluidized backflushing without the rake stirring mechanism. This helps the filter very much to be of the towery type with multilayers.

In this paper, through theoretical analysis and calculations the authors provide necessary data of fluidizing the gravel bed. The application of this filter in industry and the comparision of its technology with that of ordinary gravel-bed filters and other types of efficient dry filters have shown this filter is simple in structure and easy for maintenance. It takes up less space and requires less capital cost as well. To the present , this type of filter with gas volume I20000m^3/hr has been run in practice and its performance of reverse cleaning is satisfactory.

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A GRAVEL BED FILTER WITH FLUIDIZED-BED DURING REVERSE CLEANING

INTRODUCTION

Since the 1960s the gravel bed filters have been used for removal of dust from gas stream in some industries, such as in clinker coolers, lime kilns and sinter machines. The gravel bed filter uses solid granular materials such as granular quartz, pebble-stone, etc. as its filtrating medium that has following advantages: low cost, high temperature resistance, good wear resistance and durability. In comparison with some efficient dry filters, such as electrostatic precipitators and bag houses, the gravel bed filter is simpler in construction and is easier for maintenance, its capital cost is comparatively low. So the gravel bed filter is a kind of dust collector which promises well and will be further developed.

In iron and steel plants a large quantity of high temperature dust laden gases must be cleaned. It is important to have an economic and effective method to filtrate those dust laden gas. The gravel bed filter is especially suitable for cleaning the high temperature gases, therefore this method is well worth developing.

Safety Technology Research Institute has engaged in developing the gravel bed filter since 1974. From the beginning of the research we tried to suit this kind of filter to filtration of large quantity of high temperature dust laden gases. Under such circumstance the principal method is to place the filter layers on top of each other to form a filtrating tower, which would occupy less space. In our first pilot test case pipes were used as the shaft of turning the rake stirring device in each layer, as shown in Figure I. In the second test a shaft was set at one side of the towery filter to drive the rake stirring device in each layer with sprockets and a roller chain, as shown in Figure 2. Both of tests failed because it was too difficult to bring this construction into reality and we could only overlap 3-5 layers of filter together at most. We carried on our test, trying to construct a filter, every layer having its own motor, reductor, sprocket and roller chain that would drive the rake stirring

Figure I. Filter with case pipes as shaft to drive the rake stirring device

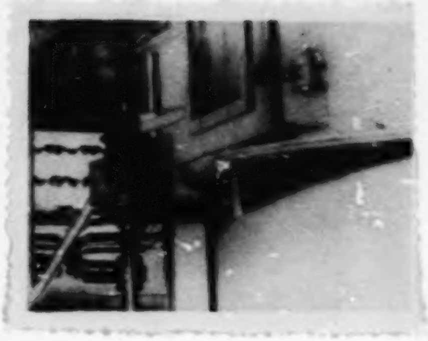

Figure 2. Filter with a side shaft to drive the rake stirring device

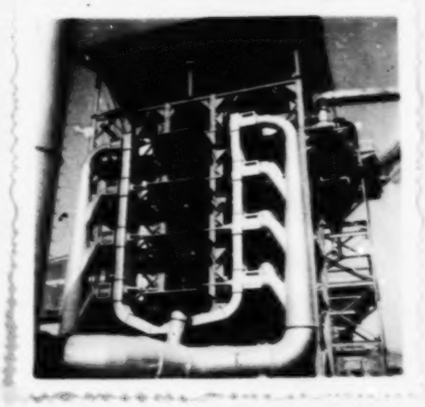

Figure 3. Filter with individual motors to drive the rake stirring device in each layer

device separately, as shown in Figure 3. However, it was still impossible for us to build such a multilayer filter tower, for the intervals between layers were too large.

Finally, by applying the principle of bulb forming and fluidization in the gravel bed, we developed in 1977 a multi-layers gravel bed filter of towery type which could clean dust remained in the filtrating bed by fluidized backflushing, so that the rake stirring mechanism could be left out. This kind of filter is much simpler in structure, easier for maintenance, occupying less space and requiring less capital cost. Now, a gravel filter of this type with gas volume 120000m^3/hr has been run in practice and its performance of reverse cleaning is satisfactory.

PRINCIPLE AND ANALYSIS

During the backflushing of the gravel bed filter with stirring rake devices, the rakes stir the granules and make them rub mutually. In this process, the backflushing air separates the dust from granules and sends the dust out of the filter layer. With the help of rake stirring, the surface of filter layers may be kept plane.

For a gravel bed filter with fluidized bed during reverse cleaning, the fluidization in the filter layer can get the same effect as the rake stirring. During the period of backflushing, the reverse cleaning air will reach a definite velocity and the filter layer will be fluidized. In the fluidized bed the granules will move up and down and rub mutually as boiling water does. In such case, dust which adheres to the granular surface may be separated and brought away by the flushing air.

To achieve ideal effect, the reverse cleaning process should be controlled as follows:

1. The bulb forming must be uniformly distributed in the whole area of the gravel bed layer, there must not be any dead corners or local blowing-off.
2. After reverse blowing, the filtrating layer must have a plane surface, on which there must be no hills, no cavities or no uneven area. Therefore the filter can achieve good filtrating effect.

3. The parts which can meet the above-mentioned requirements should be simple in construction, easy for maintenance and have high reliability and low pressure drop.

The filter layer possesses a good appearance, as shown in Figure 4 and Figure 5. In Figure 4 the filter layer is in a state of reverse cleaning. The granules move up and down uniformly as the boiling water does. Figure 5 shows that after reverse cleaning the surface of the layer of the gravel filter is quite plane.

The forming of fluidization and good reverse cleaning are determined by the size of granules, the properties of dust, the velocity of reverse air blowing, the pressure drop as well as the interval time of reverse blowing.

The Diameter of Granules

In the gravel bed filter, it is important to chcose granules of proper sizes. The diameter of granules has direct influence on the efficiancy of dust collection and reverse blowing. In general the finer the filtrating granules, the higher the dust collection efficiency and more easily the fluidization will be formed. But there are some limits to the fineness of the filtrating granules. If the granules are too fine, they would drop through the screen.

It is impossible for all the granules to have same diameter. For the purpose of denoting the size of granules, the "average equivalent diameter" Dp (mm.) is used.

Dp is determined from the following equation:

$$\frac{I}{Dp} = \sum \frac{xi}{di}$$

Where xi = the percentage of the weight of the granules whose diameter is di (mm.)

The granules are generally of irregular shape. The average equivalent diameter must be multiplied by a form coefficient φ_s to get "calculating average equivalent diameter " D_0 (mm.) which is expressed as

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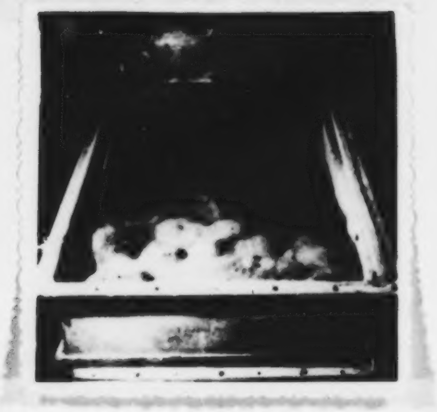


Figure 4. Filter layer in bulb forming and fluidization

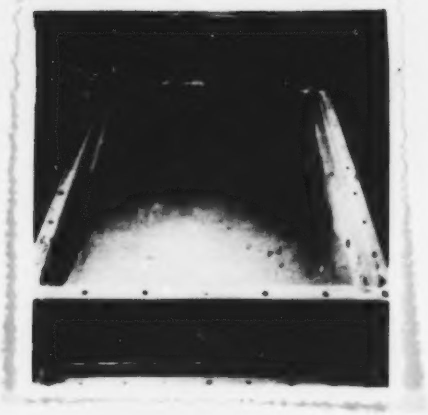


Figure 5. Filter layer after backflushing

$$D_o = \varphi_s \cdot D_p$$

The form coefficient is the root square of the ratio of spherical surface area S_s to irregular surface area S_i. It applies

$$\varphi_s = \sqrt{\frac{S_s}{S_i}}$$

Generally, the form coefficient of the granular quartz is close to 0.5 and I.3-2.2 mm. of the average equivalent diameter of granules is used.

Properties of Dust

The properties of dust, especially the adhesion, affect the result of backflushing. It is easy to blow off the dust deposited on the surface of the filtrating layer. But to blow off the dust adhering to the surface of the granules requires some specific conditions. To elutriate this kind of fine dust there must be a greater blowing-off velocity and every granule must be brought into touch with the backflushing air jet. Nowadays it has succeeded in blowing off some low adhesive dusts which adhere to the surface of the granules. But some of dust of metal oxides cannot be wholly blown off from the filter layer due to its large cohesive force.

The size of dust which can be blown off during reverse cleaning has a close connection with the velocity of reverse blowing and the density of dust itself. It may be considered that the reverse blowing velocity must be larger than the terminal settling velocity of dust particles. Only on this condition can the dust particles be blown off from the filter layer during reverse cleaning. For example, when the average reverse blowing velocity is Im/sec, only the dust whose diameter is less than 0.I5 mm. can be blown off from the filter layer, and the dust larger than 0.I5 mm. must be deposited in the settling chamber beforehand.

Critical Fluidized Velocity

When the volume of reverse cleaning air flowing through the filtrating layer is very small, the air will flow through the small porosity and the granules remain steady. This kind of filtrating layer is called steady bed. When this velocity increases, the granules begin to lift by the air. This is called primary fluidized bed. If the velocity would increase continuously, air bulb and violent stirring will occur in the filtrating filter. That is called bulbing or fluidized bed. The minimum reverse cleaning velocity which changes the filtrating bed from steady state into fluidized state is called critical fluidized velocity.

The critical fluidized velocity can be calculated by using the following equation [I]:

$$Wc = \frac{\nu}{Do} \cdot \frac{Ar\, \xi^{4.75}}{18 + 0.6\sqrt{Ar \cdot \xi^{4.75}}}$$

Where ν = kinematic viscosity (m^2/sec)
Do = calculated average diameter of granules (m)
ξ = porosity of granules layer
Ar = Archimedes number

For the porosity of granules, the following equation applies

$$\xi = \frac{\gamma_r - \gamma_b}{\gamma_r}$$

Where γ_b = bulk specific gravity
γ_r = real specific gravity of granules

The Archimedes number applies

$$Ar = \frac{g \cdot \gamma_r}{v^2 \cdot \gamma_a} Do^3$$

Where g = gravitational acceleration (m/sec^2)
γ_r = real specific gravity of granules
γ_a = specific gravity of air
ν = kinematic viscosity (m^2/sec)
Do = calculated average diameter of granules (m)

While the average equivalent diameter of granular quartz is within the range of 1.3-2.2 mm., the critical fluidized velocity will be 0.68-I.I9m/sec.

The Maximum Reverse Blowing Velocity

When the reverse blowing velocity is larger than the critical fluidized velocity, the bulbing effect will be intensive and the backflushing will achieve good cleaning result. But if the velocity of reverse blowing is too large, the granules may be blown off from the filter bed. Then there should be the maximum permissible reverse blowing velocity.

In the steady air the granules dropping due to the gravitational force has a terminal velocity. When air flow reaches this velocity, the resistance of air acting on the granules equals the gravitational force. The dropping velocity of granules would not increase further. In the field of air flow, the granules would be blown off if the velocity of air flow exceeds the terminal velocity of falling granules. So there should be the maximum reverse blowing velocity W_t(m/sec) [2] , which can be found from the relationship:

$$\frac{\pi}{6} Do^3(r_r - r_a) = \xi_g \frac{\pi Do^2}{4} \cdot \frac{r_a W_t^2}{2g}$$

In the form, ξ_g is related to the Reynolds number $Re = \frac{W_t \cdot Do}{v}$

When $Re < 0.4$

$$\xi_g = \frac{24}{Re}$$

Then $$W_t = \frac{g(r_r - r_a)}{I8\ r_a v} Do^2$$

When $0.4 < Re < 500$

$$\xi_g = \frac{IO}{Re\ 0.5}$$

Then $$W_t = \left[\frac{4}{225} \cdot \frac{(r_r - r_a)^2 g^2}{r_a^2 v} \right]^{\frac{I}{3}} Do$$

When $500 < Re < 200000$

$$\xi_g = 0.43$$

Then $$W_t = \left[\frac{3.Ig\ (r_r - r_a)}{r_a} Do \right]^{\frac{I}{2}}$$

For granular quartz its average equivalent diameter is I.3-2.2 mm.

$$W_t = 5.4\text{-}8.76\text{m/sec}$$

The Resistance of Reverse Blowing

When the reverse cleaning air keeps a low flow rate, the resistance of air flow is proportional to the air flow velocity. When the velocity of reverse cleaning air rises to the fluidizing condition, the granules will be blown up and will float in the air. The resistance of reverse blowing will be a constant. It will not increase even if the velocity of reverse blowing rises further.

In the fluidizing condition the resistance of reverse blowing "P" is close to the weight of the granular filtrating layer in unit area[I]. It is of the form

$$P = \varphi \cdot H \cdot r_b$$

Where φ = coefficient of reduction 0.8

H = height of filtrating layer (m)

Generally the resistivity of reverse blowing is in the range of I40-230mm. water.

The Cycle and Time Interval of Reverse Cleaning

Owing to the fact that the space among the granules is comparatively larger than that among the fiber in the fabric filter, the dust content in the granular bed is also larger. The pressure drop of filtrating will gradually increase when the dust in the filter layer gradually increases. We can determine the cycle of backflushing when the pressure drop of filtrating reaches a certain allowable value.

According to the experiment of filtrating for different dust concentration, the cycle of reverse cleaning may be of 4-4 3 min.

To remove the dust in the filtrating layer and to achieve good cleaning effect, it is necessary to have sufficient time interval. But the time interval should not be too long, otherwise the power consumption will tend to increase. Generally 5 seconds for the time interval of backflushing will do.

CONSTRUCTION

A typical multilayer gravel bed filter with fluidized-bed during reverse cleaning is shown in Figure 6.

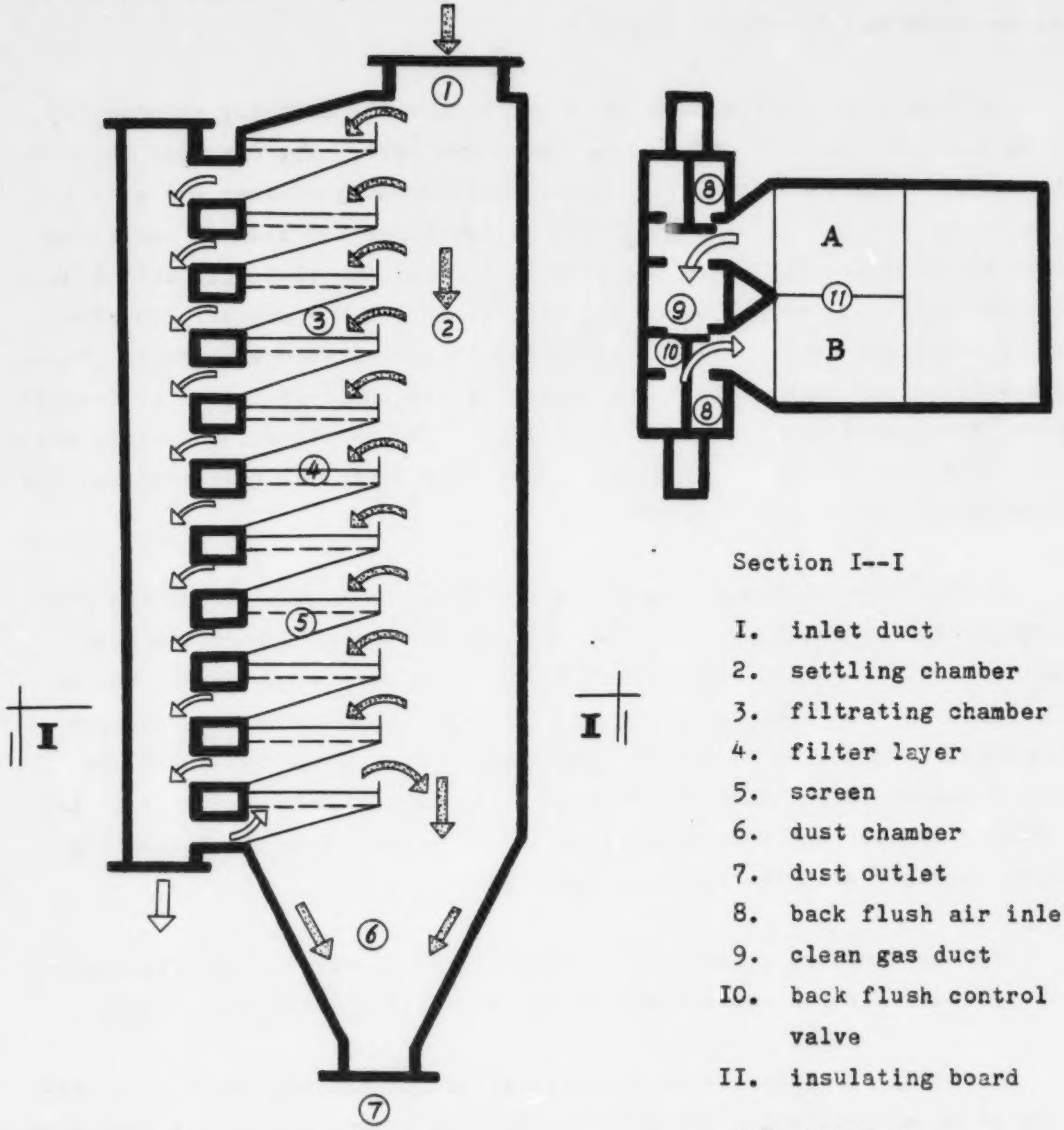
In Figure 6, the raw dust laden gas enters the settling chamber (2) from the inlet duct (I) to remove the coarse dust. The dust not deposited in the settling chamber will go into the filtrating chamber (3) with the gas, where the gas flows through the filter layer (4) and the remaining dust is removed. Filtrated gas then will enter the clean gas outlet duct (9) through the screen (5) and the exhaust port. The process described above continues until the filtrating bed is fully laden with dust. Then a new cleaning cycle begins. At this time the layer of filter is isolated from the cleaned gas stream by actuation of the backflushing control valve (IO) driven by the valve cylinder. Then this layer has come into the bed cleaning or backflushing period.

In the lower filtrating layer in Figure 6, fresh air enters the unit through the backflushing air inlet (8) and is carried upward and runs through the filtrating layer (4). During this period the gravel bed is fluidized so that stirring bulbs are formed. The dust is removed from the filter medium. Some of the agglomerated dust particles which are significantly larger than the original fine dust will be led down to the settling chamber and some other dust is reintroduced to the filtrating layer together with the raw dust laden gas.

The backflushing valves are powered by the double-acting compressed air cylinders, which are controlled by an adjustable interval timer.

A section of filter layer consists of two filtrating areas (A.B) separated by an insulating board (II). All the layers are of the same construction. Consequently it is easy to place one layer over another. Generally 4 layers are combined to be a set, and a multilayer towery type gravel bed filter consists of several sets.

The chief advantages of the gravel bed filter with fluidized-bed over the ordinary gravel bed filters are as follows:



Section I--I

I. inlet duct
2. settling chamber
3. filtrating chamber
4. filter layer
5. screen
6. dust chamber
7. dust outlet
8. back flush air inlet
9. clean gas duct
IO. back flush control valve
II. insulating board

A.B filtrating area

Figure 6. Schematic diagram of multilayer gravel bed filter with fluidized bed during reverse cleaning

Due to the omission of the rake stirring mechanism the construction of the filter is simplified and the height of every layer is effectively reduced. Then it is easy to build the towery type of gravel bed filter. In the filtrating chamber, the temperature resistivity is improved and the maintenance needs less labour. Now the principal part of a filter with gas filtrating volume 30000m^3/hr only occupies an area of I6m^2, and only costs RMB I200 Yuan per I000 cubic meters of dust laden gas an hour.

APPLICATIONS

The gravel bed filters with fluidized bed during reverse cleaning have been installed in the following areas.

Sintering Plant

The first gravel bed filter of this type was installed in a sintering plant in I979, as is shown in Figure 7. This filter is used to filtrate the dust laden gas in an agglomerat transportating and lifting system. There are altogether I0 filtrating layers. This filter can treat I5000 cubic meters of dust laden gas an hour. For the dust of agglomerat 75% of which was less than 40 μ in diameter, the filter can have 95-97.8 percent filtrating efficiency. The temperature of raw gas was I30-I80°C. The pressure drop of the filter is about 80mm. water.

The second set of this type filter installed in I980 is used for controlling the smoke of a sintering machine, Figure 8. It has 22 filtrating layers and can treat 25000-30000 cubic meters of duct laden gas an hour. For the dust 72.8% of which is less than 40 μ in diameter, the filter can have 96 percent collection efficiency. The temperature of raw gas is I50-I70°C. The pressure drop of the filter is about 80-90 mm. water.

Steel Heating Furnace

In October I978, a filter of this type with I8 layers was installed in a steel heating furnace. In April I979 three more filters of the same type were installed at the same place, as is shown in Figure 9. The total volume of dust laden gas filtrated by these four filters is I20000m^3/hr. For the dust 9I.2% of which is less than 40 μ in diameter, 95 percent col-

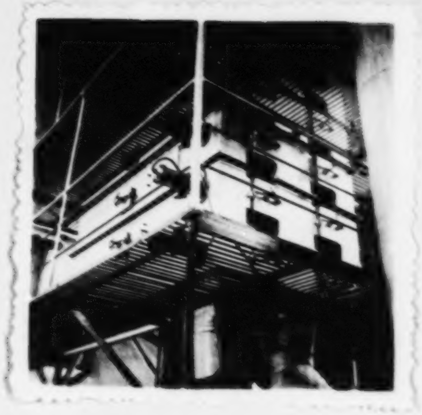


Figure 7. Filter installed in an agglomerat transportation and lifting system

Figure 8. Filter installed in a sintering machine

Figure 9. Filter installed in a steel heating furnace

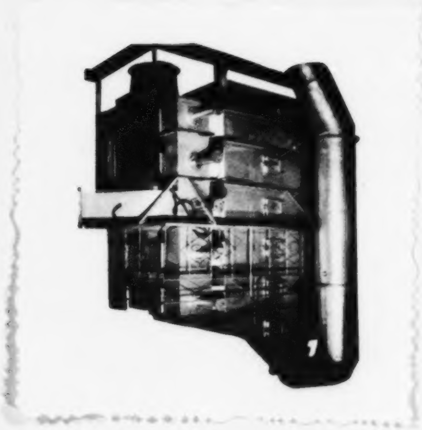


Figure 10. Filter installed in a clay drying machine

lection efficiency can be reached. The temperature of raw gas is 217C. The filtrating medium is granular quartz. The filter layer is 110-150 mm. high. The pressure drop during filtration is 70mm. water.

Clay Drying Machine

A gravel bed filter of fluidized backflushing with 10 layers was installed in a clay drying machine in 1978, as is shown in Figure 10. The gas volume of this filter is 15000m^3/hr. The collection efficiency is 98-98.5%.

CONCLUSION

From the experiments and practical operation of the gravel bed filter with fluidized-bed during reverse cleaning, the authors have come to the following conclusions:

1. When the velocity of backflushing is slightly greater than the critical fluidizing velocity, air bulbs and violent stirring take place in the granular filtrating layer. After backflushing the surface of filtrating layer can keep plane and the dust which sticks to the granular surface can be removed. The primary pressure drop of the filter recovers.

2. By applying the theory of fluidization to backflushing, the gravel bed filter can be constructed without the rake stirring mechanism. It is easy for this kind of gravel bed filter to be of multilayer towery type, more applicable to the filtration of large quantity of high temperature dust laden gas in iron and steel smelting plants.

3. Compared with the conventional gravel bed filters, the gravel bed filter with fluidized-bed during reverse cleaning is much simpler, requires less capital cost and occupies less space. It is easier for maintenance and owns good heat resistance.

To raise the dust collection efficiency and to filtrate adhesive dust with this kind of filter, we still have much to do.

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The End

FINE PARTICLE CONTROL AT HIGH GAS TEMPERATURE

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ABSTRACT

A new filter media made from ceramic fibers offers the potential for fine particulate control at gas temperatures up to 1,000°C (1,800°F). These filter media represent an emerging technology under development for application to hot gas cleaning in pressurized fludized bed combustion. However, the ability to control particles at extreme temperatures will offer benefits to other industries as well. For example, the 1,000°C filter will reduce the need to dilute hot gas streams in the iron and steel industry prior to particle removal. The resulting clean hot gas can then be used in a heat recovery system to offset the cost of pollution control. Progress to date in the development of this new filtration device is reviewed in this paper.

FINE PARTICLE CONTROL AT HIGH GAS TEMPERATURE

INTRODUCTION

Pressurized fluidized bed combustion and some other advanced coal utilization processes contain particle laden hot gas streams (800°C). Before energy can be extracted from these gas streams, the particles must be removed to protect the energy extraction equipment -- usually a turbine. Because of their simplicity, cyclones are a preferred device to accomplish this particle removal and up to three cyclones in series have been used with promising results on cascade erosion tests. But, cyclones do not remove fine particles (<5 μm) which are a potential health hazard and will need to be removed before release to the atmosphere. In addition, potentially corrosive alkali metals are concentrated in the fine particle fraction of the dust distribution and could damage metal turbine components through deposition on the blading. Thus, if it were economical to do so, there are technical advantages to removing all particles, including fine particles, from the hot gas stream. The ceramic fiber filter media under development at Acurex offers the potential to accomplish this needed fine particle control at high temperatures.

The ceramic filter represents a system approach to filter design. That is, it is not simply a material substitution of ceramic fibers for conventional fibers. The entire filter unit including media support and cleaning techniques are designed for the unique properties of the ceramic fibers. This approach maximizes the advantages of ceramic fibers while minimizing the effects of their weaknesses. The media employs fine diameter fibers (3 μm nominal) which provide improved collection efficiency. Fibers are arranged in a mat having a low solidity so that they can move relative to one another. This prevents breaking of individual fibers during cleaning. A loosely woven ceramic cloth on the inner and outer surfaces of the media provides a strengthening screen which contains the filtration layer of fine fibers. Because the media is inherently more efficient than conventional media, dust tends to deposit and form a cake on its surface where it is most easily removed. It can also collect particles at relatively high face velocity 10 cm/sec (20 ft/min). Operation at high face velocity requires offline cleaning to prevent reintrainment of the dust removed by the cleaning pulse. Cleaning offline also provides the most effective cleaning at minimum energy. To provide continuous filtration only a portion of the filter unit is cleaned at a given time.

Significant features of the ceramic filter are:

- Operation at high temperatures and pressures (800°C nominal, up to 10 atm or more pressure)
- High efficiency collection of fine and submicron particles offers potential for alkali removal
- High face velocity operation offers potential for compact size and lower costs
- Pressure drop is determined primarily by dust cake properties and face velocity

The Acurex ceramic filter has been shown to be a promising concept for hot gas cleaning in a series of feasibility tests sponsored by the Environmental Protection Agency (EPA). The results of those tests are briefly reviewed in this paper.

THEORY DISCUSSION

The equations predicting filter performance show that fiber diameter is an important parameter. Small diameter (3 μm) fibers improve performance but, except for very high efficiency filters as used in biological applications, fine fibers have generally not been used in filter media design. The principle reason is that fine fibers are not commercially available as readily as coarser (20 to 50 μm) fibers, such as cotton or cellulose. Since the textile industry dominates the use of fibers, most artificial fibers have been made to simulate natural ones. Also small fibers are more expensive to produce and existing fibers perform satisfactorily in most cases. So, even though seldom used, fiber diameter is a powerful tool to manipulate filter media performance.

Space limitations do not permit a complete analytical discussion of temperature and pressure effects upon filter performance and of how these effects can be overcome in the design of a filter media. These analyses have been made, however, and the results are summarized below.

Because of the increased viscosity of gases at high temperatures, particle collection by inertial impaction is reduced 10 to 15 percent for the particle size range of 0.5 to 5.0 μm. Thus, an inertial device collecting 2.0 μm particles at 90 percent efficiency in a room ambient test may collect the same particles at only 75 percent efficiency at high-temperature and high-pressure (HTHP) conditions.

Filters employ inertial impaction, direct interception, and diffusion mechanisms in collecting particles. High-temperature and pressure influence collection by diffusion only slightly and may, in fact, improve performance. Direct interception is not a function of temperature and pressure. All three of these particle collection mechanisms, however, are strong functions of fiber diameter. If the predicted performance of a fiber bed composed of 20 μm diameter fibers is compared with an equal weight per unit area of 3.0 μm diameter fibers, collection efficiency will significantly improve. This improvement in performance will be much larger than the adverse effects resulting from operation at high temperatures. For example, such a change in fiber diameter will improve collection of 0.5 μm particles from 20 percent using 20 μm fibers, to almost 90 percent using 3.0 μm fibers. Filters achieving 20 percent collection of 0.5 μm particles are typical of those in commercial use and their adequate performance can be attributed to the additional filtration efficiency of the dust cake which forms on the filter surface. Thus by using small fibers and by relying upon dust cake filtration, it is possible to make a filter media which will give good performance at viscosity conditions similar to those at high temperatures.

Fortunately ceramic fibers are available which have diameters of 3.0 μm. Figure 1 presents the performance predicted for a bed of 3.0 μm

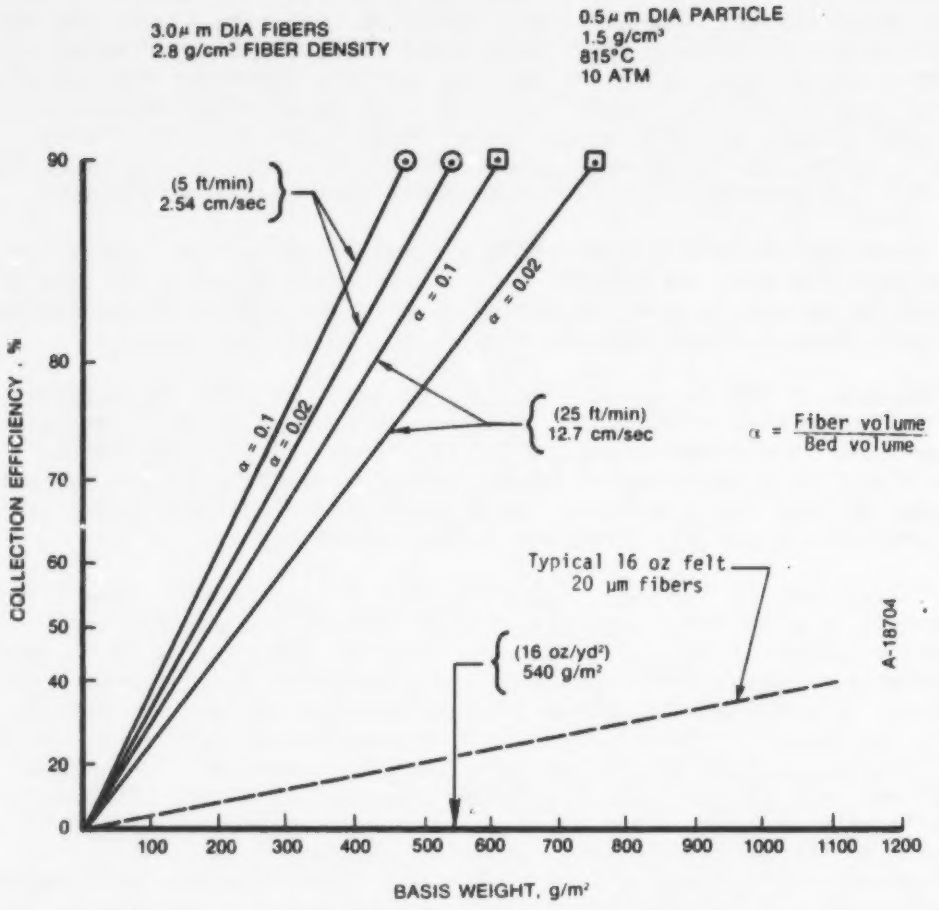

Figure 1. Calculated performance of a ceramic fiber bed composed of 3.0 μm diameter fibers.

ceramic fibers and 16-ounce felt collecting 0.5 μm particles under HTHP conditions. The felt is a conventional filtration media with 20 μm fibers. It is apparent that an equal weight of fine fibers causes dramatic improvement in collection efficiency.

Some other useful observations can be made from Figure 1. The effect of filter face velocity and filter media solidity on efficiency are small compared to the effects of the change in fiber diameter. In other words, a filter composed of 3.0 μm fibers could have higher collection efficiency than currently used commercial filter media, even if operated at filter face velocity as high as 25 ft/min and if only 2 percent of the bed were occupied by fibers (98 percent open area). The figure also shows that collection efficiency can be increased by adding fibers (increasing the basis weight). This is, in effect, what happens when a dust cake is formed -- the dust cake gets thicker and collection efficiency and pressure drop increase.

In summary, currently available fiber filtration models show that fine fibers employed in a mat filter will be able to achieve high efficiency collection of fine particles under high-temperature and pressure conditions. Further, that a low solidity (fluffy) bed of these fibers can achieve high efficiency fine particle collection even at filter face velocities as high as 25 or 30 ft/min. Our test programs have verified these theoretical results.

This discussion has only addressed particle collection. Other important questions concerning operating pressure drop, durability, and cleanability are best examined by experiment and are discussed in the following section.

SUMMARY OF TEST EXPERIENCE

Four categories of feasibility tests have been performed:

- Room ambient tests -- These tests confirmed the theoretical analysis and examined a broad spectrum of ceramic filter media candidates
- High-temperature and pressure mechanical durability tests -- These tests determined that the ceramic filter media candidates could survive the mechanical stresses associated with 50,000 cleaning pulses (about 1 year of service)
- High-temperature and pressure filtration tests -- These tests measure the filtration characteristics of the filter media in 200-hour dust feeding tests
- Slipstream tests at PFBC -- These tests showed high collection efficiency and cleanability of a ceramic fiber filter in tests at the EPA/Exxon Miniplant using as-generated PFBC flyash which passed the secondary cleanup cyclone

Room Ambient Filter Media Tests

A large number of ceramic fiber filter media candidates were subjected to a series of filtration tests at room ambient conditions. These tests included some examples of conventional filter media for comparison. The type of tests performed were:

- Dioctylphtalate (DOP) smoke penetration as a function of airflow velocity
- Determination of maximum pore size (in micrometers)
- Measurement of permeability
- Flat-sheet dust loading tests using AC fine test dust (a standard 0 to 80 μm classified Arizona road dust). Overall collection efficiency and dust loading required to develop 3.7 kPa (15 inches H_2O) pressure drop are determined from this test which is run at 10 cm/sec (20 ft/min) face velocity.

The test data revealed which of the available ceramic media candidates would most likely provide good filtration performance. These data are shown in detail in EPA-600/7-78-194. A summary of findings from these tests follows:

- Several of the ceramic paper and felt materials are capable of removing fine particles at high efficiency without excessive filter basis weights. DOP tests tended to confirm the performance predicted by analysis as shown in Figure 1.
- The ceramic paper and felt materials have filtration characteristics and performed similarly to paper and felt commercial filter media in a series of filter media tests
- The ceramic woven materials were characterized by large pores and low collection efficiency in the dust loading tests. The range of parameters exhibited by the various woven materials indicates that an acceptable woven ceramic filter media can probably be fabricated. However, acceptable performance would only occur at low air-to-cloth ratios.
- "Blanket" ceramic fiber materials (felts) consisting of small diameter fibers (3.0 μm) appear to be the most promising materials for high temperature and pressure tests because of their combination of good filtration performance and relatively high strength

High-Temperature and Pressure Mechanical Durability Tests

The mechanical durability tests answered the following questions:

- How durable are ceramic fiber structures when subjected to environmental conditions associated with filtration applications?
- How well do ceramic fibers perform as filters in the HTHP environment?

Concerning the first question, three ceramic filter media configurations survived a test during which the filter elements were subjected to 50,000 cleaning pulses. The objective of these tests was to simulate approximately 1 year of operation of mechanical cleaning loads on the media at high-temperature and pressure. These tests showed that the low solidity, fine-fiber filters were undamaged by pulse cleaning loads. They also showed that the flyash dust cake was deposited mostly on the surface of the media. Details of these tests were also reported earlier and in EPA-600/7-78-194.

High-Temperature and Pressure Filtration Tests

Filter performance at high temperatures and pressure was tested for a period of 200 hours. The filter media configuration which was selected as most promising consists of an approximately 1 cm thick layer of Saffil alumina blanket insulation material. This ceramic material was contained between two layers of knit 304 stainless steel screen and provided a basis weight of approximately 500 g/m^2. Tests were performed at three airflow velocities to determine performance as a function of both time and filter media face velocity. Reintrained flyash from the EPA/Exxon Miniplant was used as the test dust. Figure 2 presents average outlet concentration as a function of time for the three tests which were performed. The designation "Turbine Limit" corresponds to the turbine tolerance of 0.002 gr/scf reported by Sverdrup in EPA-600/9-78-004. During the three tests, between 40 and 100 kg of dust was fed to each test filter. Each test filter contained only 1.5 ft^2 of filter media area, so dust loading was considerably higher than that expected from the second stage cyclone of a typical PFBC. During these tests, cleaning pulses occurred about once every 10 minutes and pressure drop was maintained at less than 10 inches of water. The test conducted at 2.5 cm/sec airflow velocity showed an increased rate of penetration after about 50 hours of operation. This condition evidently was caused by a defect in the filter media although subsequent visual examination could not positively locate this defect.

Outlet concentration as a function of face velocity (air-to-cloth ratio) is plotted on Figure 3 for three time periods of 50, 100, and 200 hours. If we assume the filter used in the first test at 2.5 cm/sec developed a leak and extrapolate expected performance (dotted lines), it is apparent that outlet concentration is reduced as a function of time at all velocities. This result is similar to that of using conventional filter media in a room ambient dust feeding test.

Overall particle collection efficiency is plotted as a function of face velocity (air-to-cloth ratio) on Figure 4 for three time periods of 50, 100, and 200 hours. Again, if the two discrepant data points are ignored, collection efficiency is essentially independent of face velocity in the range tested. This is consistent with a hypothesis which holds that filter penetration occurs primarily during cleaning. The filter was cleaned at zero forward flow in all three tests (offline).

Slipstream Tests at the EPA/Exxon Miniplant

A 1.5 ft^2 ceramic bag filter was evaluated/at the EPA/Exxon Miniplant PFBC. The results summarized below were reported in the January 1979 Monthly Progress Report No. 107 for EPA Contract 68-02-1312, under which Exxon Research and Engineering Company operated the miniplant test rig.

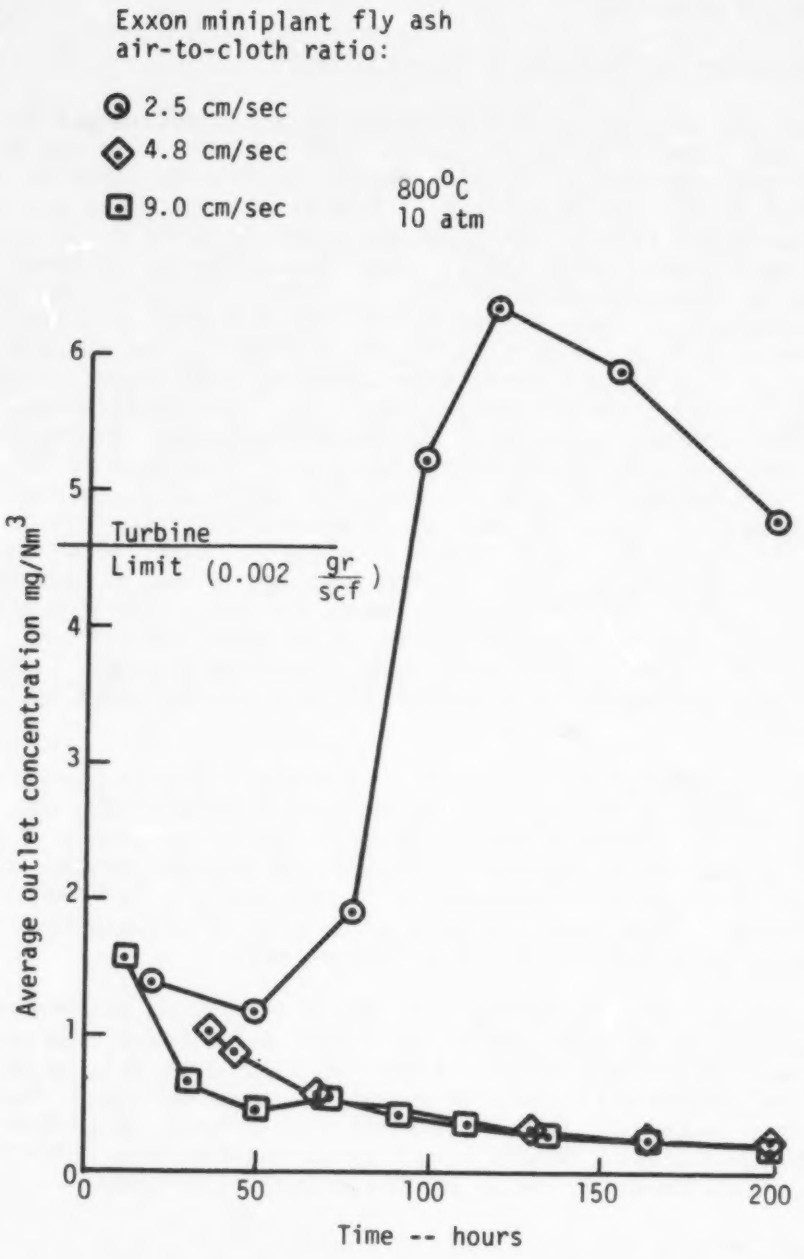

Figure 2. Average outlet concentration.

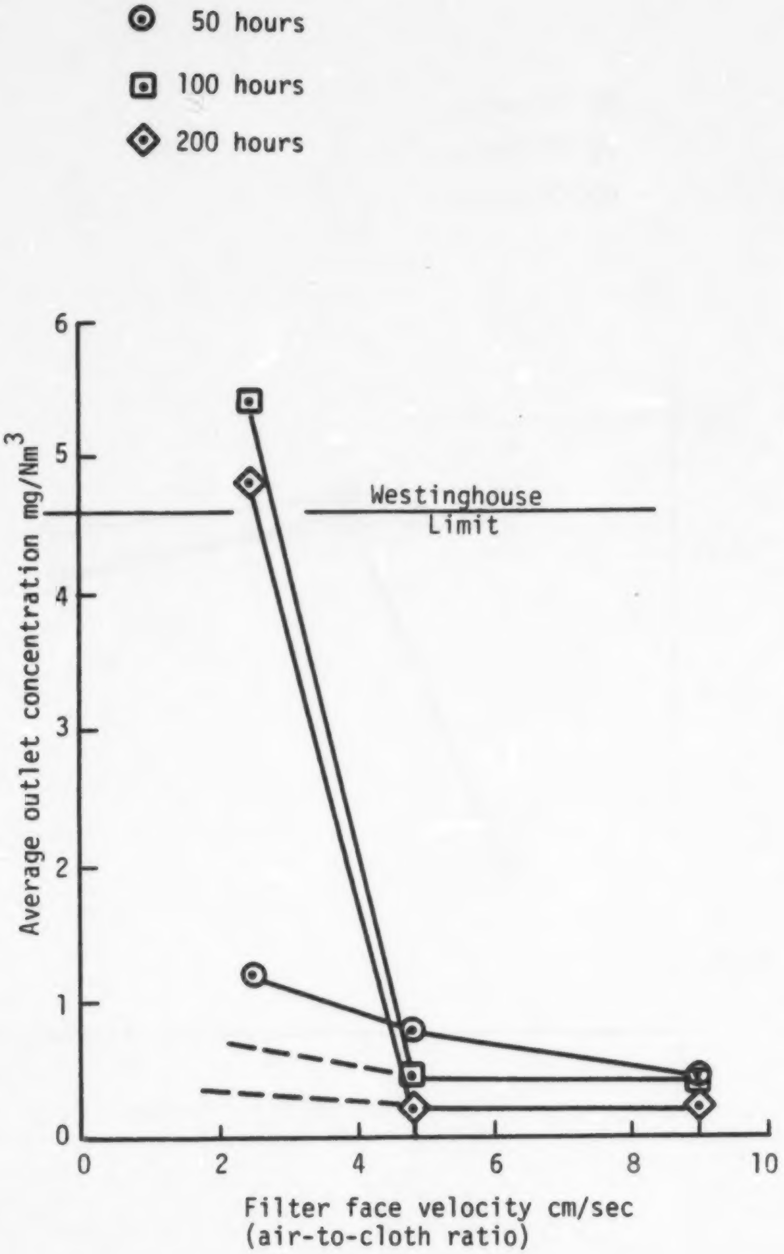

Figure 3. Outlet concentration as a function of face velocity.

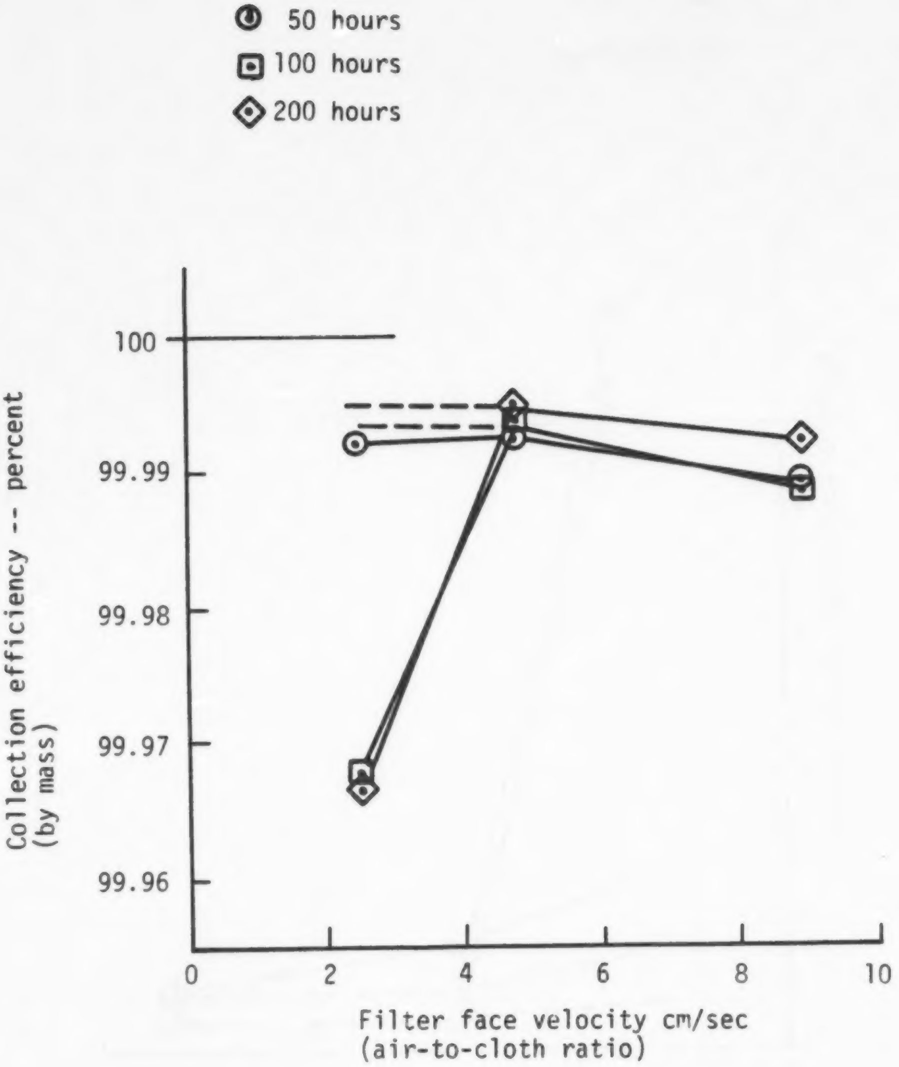

Figure 4. Collection efficiency as a function of face velocity.

The pressure drop across the filter bags varied with time in the classical manner for fabric filters Figure 5 which demonstrates that the bags could be cleaned. The effect of coal type on cleanability seemed to be fairly small, and could not be determined from the relatively few tests completed at the miniplant.

Filtration efficiencies for the Acurex ceramic bag filter were all over 90 percent, generally ranging from 96 to 99.5 percent. An exact filtration efficiency was difficult to determine because of problems in measuring the filter inlet particle concentration. Filter inlet particulate concentrations were measured or calculated by three methods: (1) Balston total filter catch on an extracted sample, (2) mass balance around the third miniplant cyclone, (3) mass balance around the ceramic bag filter.

The bag filter outlet particulate concentration was determined by passing the entire filtered gas flow through a large Balston total filter. The total particulate concentration was obtained by weighing the filter before and after collection. A particle size distribution could not be obtained. The concentration of particles on the total filter was so low that insufficient material was available as a filter cake for Coulter Counter analysis. The filters were washed off with a solvent (Isoton II) in an attempt to remove particles without mechanical brushing. This method allowed enough Balston filter material to be washed into solution to completely obscure the flyash particulates. A clean Balston total filter, not exposed to any flyash but also washed with Isoton II gave a sample which had a size distribution similar to that obtained from a used filter.

During the tests at the miniplant, one double and eight single-thickness bags were exposed to PFBC conditions. Most bags were exposed for 6 hours or more. By averaging the face velocity and exit particulate concentration over the first 6 hours of new bag exposure a plot of velocity against loading yield points closely clustered around a line Figure 6. The effect of coal type on outlet loading was insignificant.

The outlet particulate loading tended to decrease with increasing exposure time. Figure 7 shows the change in outlet loading with time. Along with the decrease in filter particulate outlet loading, baseline pressure drop increased from 0.1 to 3.0 kPa as expected. The filter cake, which was not completely removed with cleaning, caused both the lower outlet loading and the higher pressure drop.

Bag cleaning at ambient conditions after a run was not a problem. Several of the filter elements were cleaned by passing a vacuum hose over a strip of the element. This strip had the appearance of a virtually new bag, indicating very little dust penetration through the bag fibers.

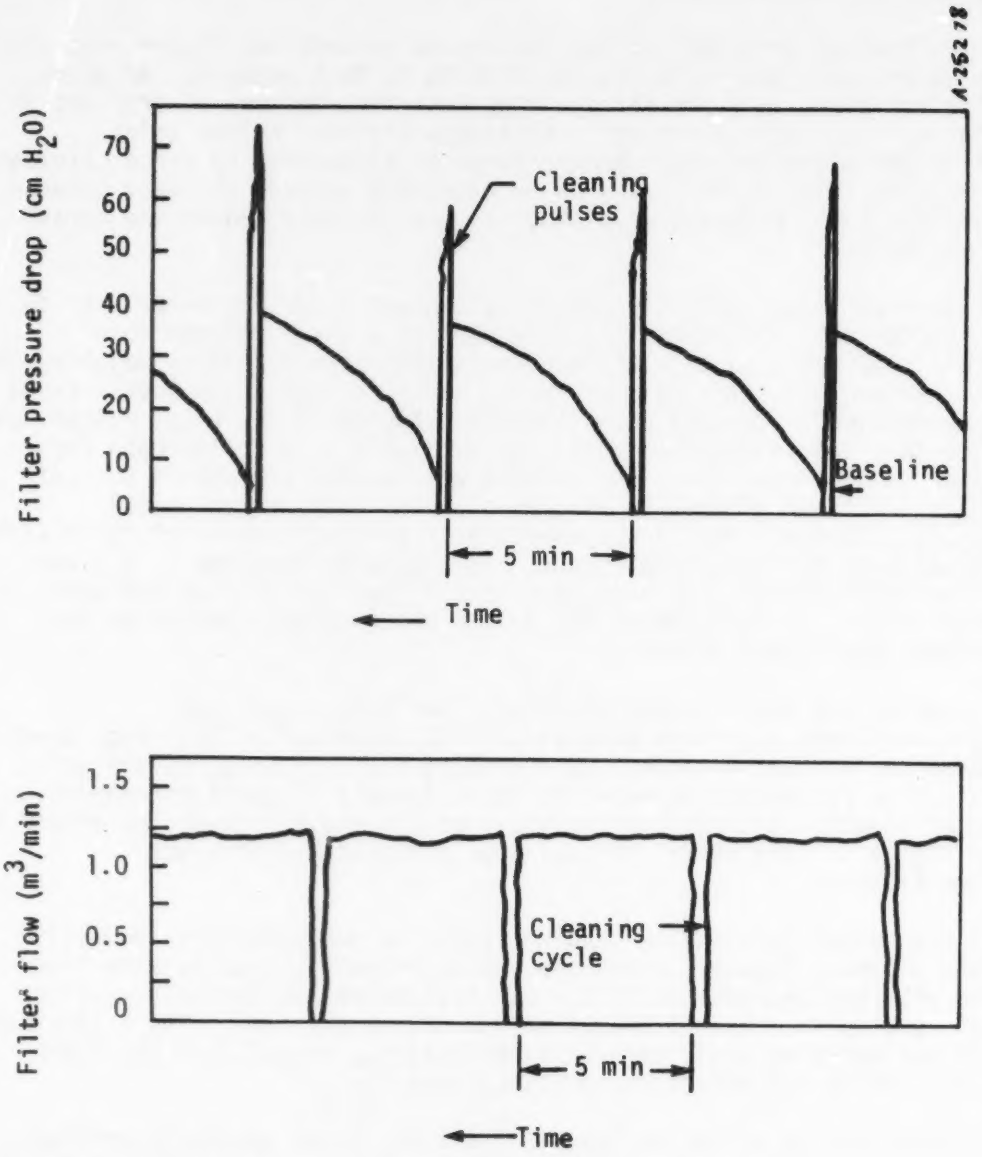

Figure 5. Acurex HTHP ceramic bag filter pressure drop and flow.

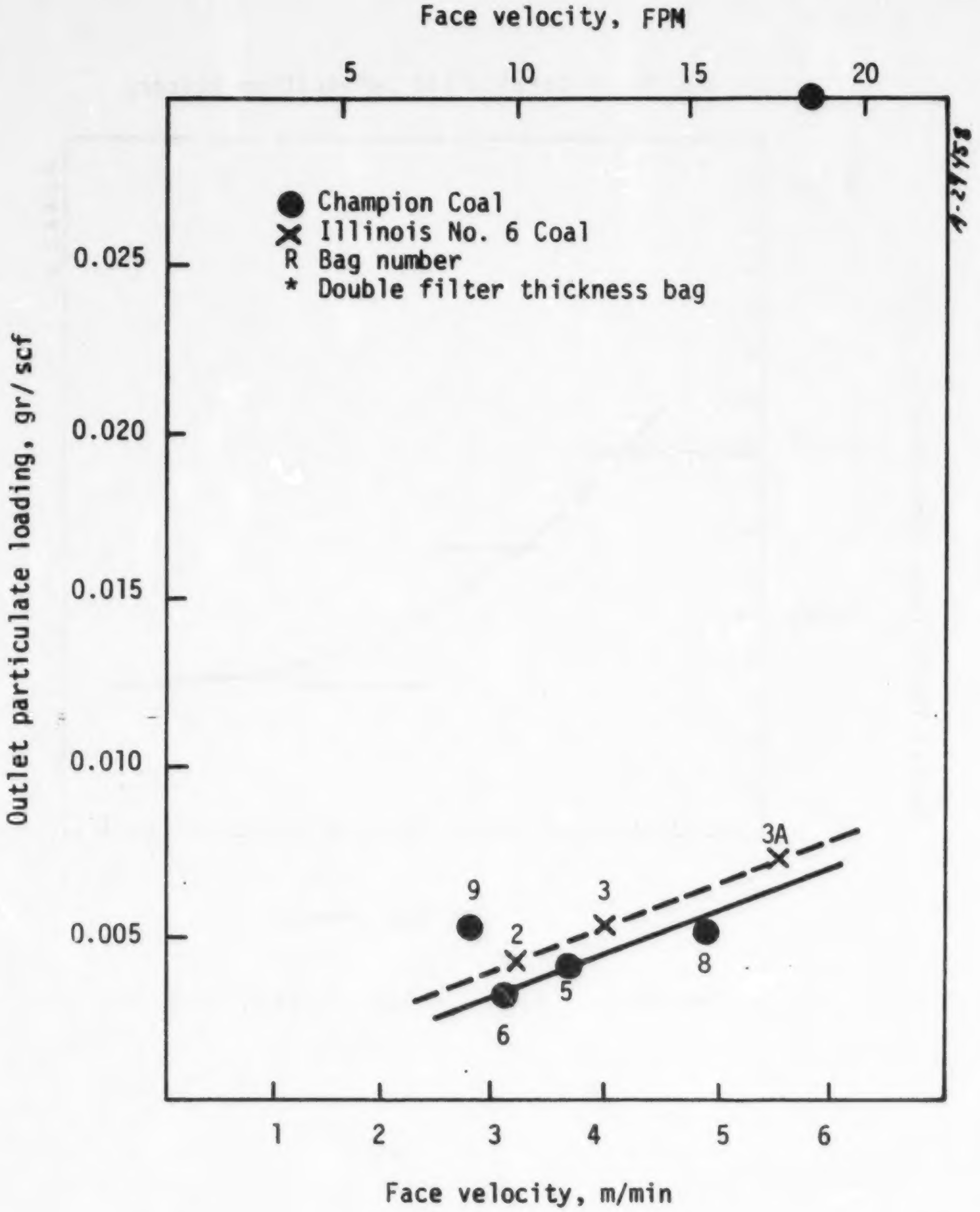

Figure 6. Acurex HTHP bag filter outlet loading vs. face velocity (averaged over first 6 hours of exposure).

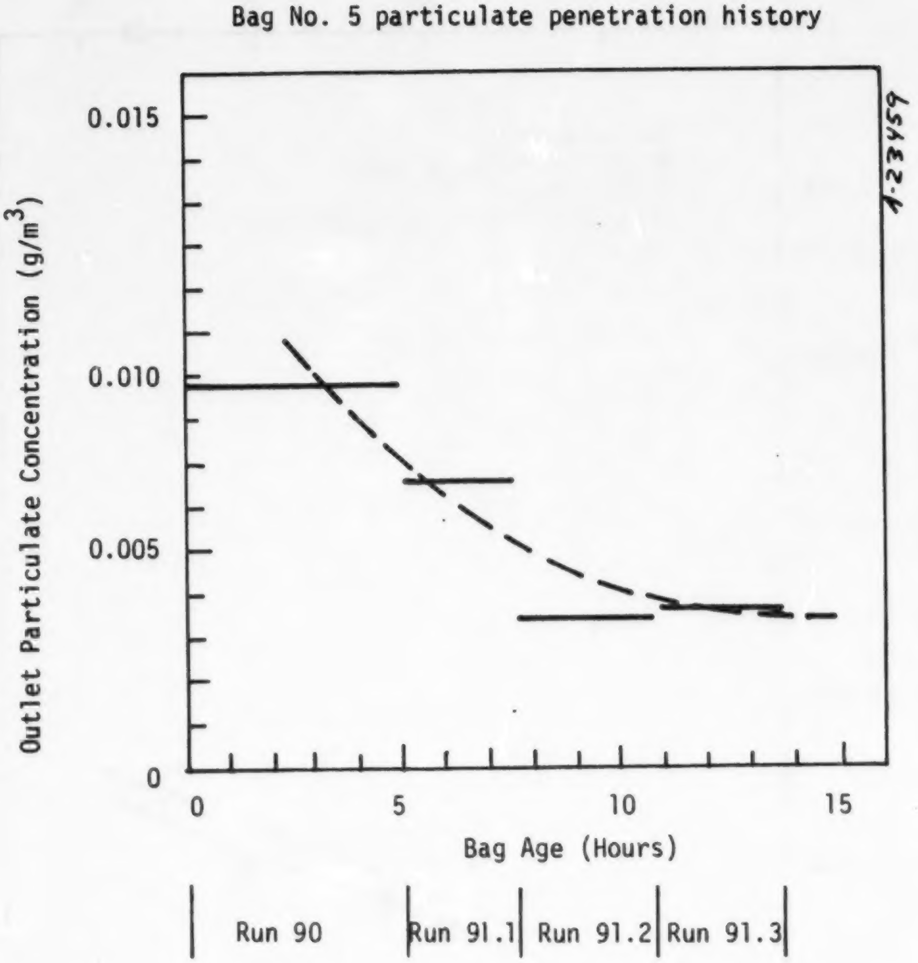

Figure 7. Acurex ceramic bag filter -- bag no. 5 particulate penetration history.

At its conclusion, the Exxon report said:

"Based on these preliminary tests, high-temperature, high-pressure ceramic bag filtration appears to be feasible. Pressure drops of under 2 kPa have been maintained for over 6 hours at face velocities of 4.6 m/min with efficiencies of 95 to 99 percent. The short evaluation tests have yielded results far superior to granular bed filtration which never achieved efficiencies greater than 95 percent and which also had baseline pressure drops in excess of 14 kPa. Further testing is required to determine maximum economic face velocity, and bag life under optimum cleaning conditions."

A larger ceramic filter test unit containing five filter elements each 1.5 m (5 ft) long and having 2.3 m^2 (50 ft^2) of filter area has been built for testing at Westinghouse under an EPRI-sponsored test program. Results of this testing will be reported at a future date.

Through the cooperation of the EPRI, a swatch of the ceramic filter media was exposed to the hot dusty gas from the PFBC at the CURL facility in Leatherhead, England during a 1,000-hour test there. While this was not a filtration test, subsequent examination of the fibers revealed that no damage resulted from 1,000 hours of exposure to the chemical products of combustion of coal.

SUMMARY AND CONCLUSION

Through a series of tests conducted at laboratory bench-scale and on a slipstream of gas at the EPA/Exxon Miniplant, the Acurex ceramic fiber filter has continued to show that a cleanable filter capable of operation at up to 800°C (1,500°F) can be developed to commercial scale. Evidence in support of this conclusion includes:

- A theoretical basis exists for it
- Room ambient tests showed high efficiency collection of fine particles
- Room ambient tests showed dust cake formation and dust loading characteristics similar to conventional media
- Accelerated pulse cleaning tests showed the media could survive mechanical flexing associated with 50,000 cleaning pulses at 800°C (1,500°F)
- Dust loading tests at high temperature and pressure with flyash showed that high collection efficiency and good cleanability (control of pressure drop) could be maintained for 200 hours at face velocity up to 10 cm/sec (20 ft/min)
- Tests on a slipstream of gas at the EPA/Exxon PFBC miniplant showed the filter could perform satisfactorily in removing particles of flyash from an as generated gas stream
- 1,000 hours of exposure to hot PFBC gas and dust showed the media could survive the chemical environment of the PFBC exhaust

Continued development of the ceramic filter is planned under a DOE-sponsored program which will culminate in a subpilot-scale demonstration at the experimental PFBC operated by Curtiss Wright Corporation in Woodridge, New Jersey. Successful completion of this program will provide a capability to control particles including fine particles at temperatures of 800° to 900°C (1,500° to 1,650°F) and pressures of atmospheric to over 10 atmospheres. This will provide protection for gas turbines in PFBC applications and may eliminate the need for further cleanup of the effluent gas stream and result in lower total installation and operating costs. In addition, the filter should find application in heat recovery and in industrial processes for high-temperature particle control.

BOF AND Q-BOP HOT METAL CHARGING EMISSION COMPARISON

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ABSTRACT

Fumes generated during hot metal charging of a BOF and a Q-BOP were sampled and analyzed for total particulates, particulate mass in four size ranges, and inorganic and organic compounds. The data indicate that the Q-BOP generates three times as much particulate and 15 times as much organic matter per megagram of hot metal charged as does the BOF. Polynuclear aromatic hydrocarbons (PNA) were found in the Q-BOP fume but not in the BOF fume. No carcinogenic PNAs were detected.

The differences found are probably due to the additional time required to charge hot metal into the Q-BOP at the particular plant sampled as compared to the BOF (2.2 minutes for the Q-BOP versus 1.0 minutes for the BOF) and to blowing of nitrogen gas into the bottom of the Q-BOP during the charging operations.

BOF AND Q-BOP HOT METAL CHARGING EMISSION COMPARISON

INTRODUCTION

This paper summarizes results obtained in two studies[1,2] of fumes generated during hot metal charging of basic oxygen furnaces. Two types of vessels were tested. One, referred to herein as the BOF, is of typical design in that oxygen is introduced during the "blow" period through a lance suspended above the metal. In the second vessel, referred to as the Q-BOP, oxygen is blown into the vessel through tuyeres in the bottom of the vessel. A gas, usually nitrogen, is blown into the vessel through the tuyeres at all other times to prevent their plugging.

The purpose of the testing was to determine if, and in what amounts, a wide variety of inorganic and organic materials might be generated during the hot metal charging and to determine if there is a significant difference between vessel types. Although both furnaces tested do have equipment operating to collect and control the emission of these fumes, no testing was done on the outlets from the control equipment. All testing was of the uncontrolled fume going to the emission control equipment.

Samples of the fume generated during hot metal charging were collected using the Source Assessment Sampling System (SASS). This system, shown in Figure 1, collects particulate matter in four size fractions (>10 μm, 3-10 μm, 1-3 μm, and <1 μm). It also traps organic vapors with an organic resin (this section of the train is referred to as the organic module) and certain metals (mercury, antimony, and arsenic), that may be in the vapor phase, using a series of impingers.

I will first briefly discuss the two vessels and the testing conducted on each. A direct comparison of the results obtained will then be presented.

Q-BOP TESTING

The Q-BOP shop tested contains two vessels each rated at 225 tons/heat. Six to eight heats can normally be completed in an eight hour shift. Shown in Figure 2 is a schematic of the Q-BOP vessel and ancillary equipment. The Q-BOP vessel differs from the conventional BOF in that oxygen is introduced through tuyeres in the bottom of the vessel rather than through a lance above the charged metal. When the vessel is being charged nitrogen gas is blown

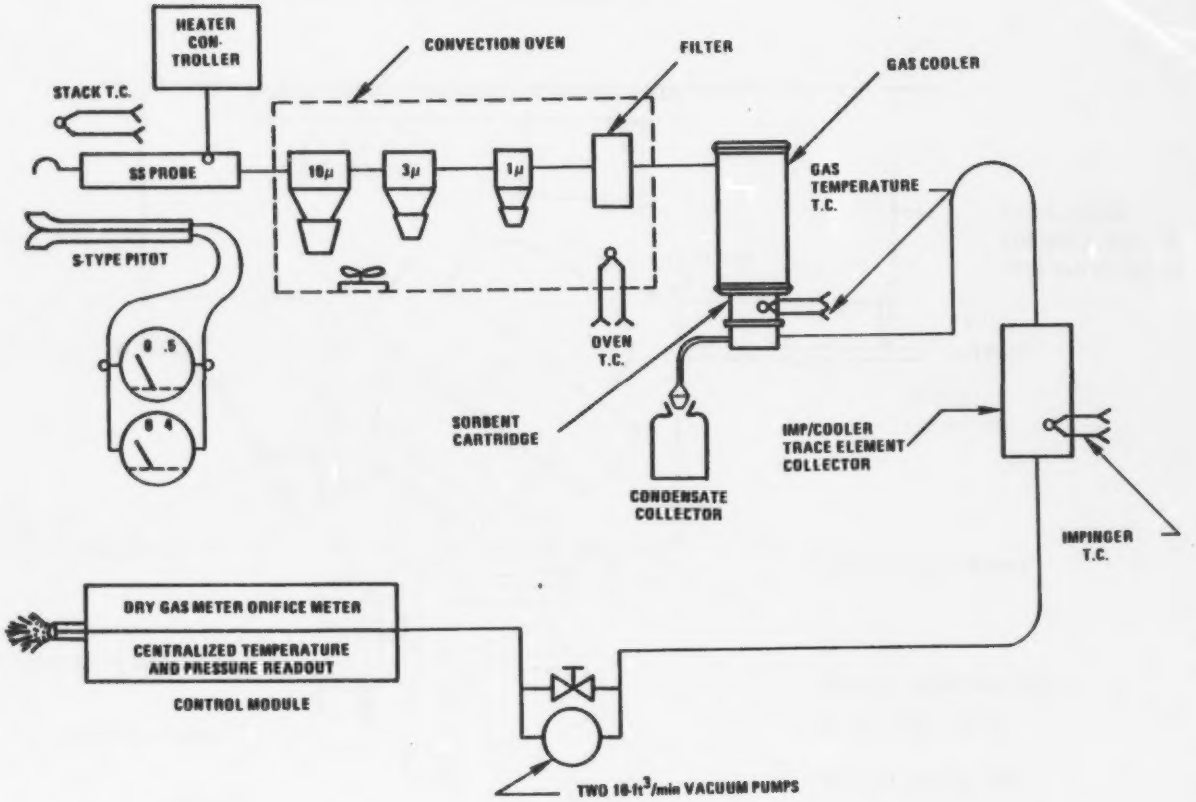

Figure 1. Source assessment sampling system.

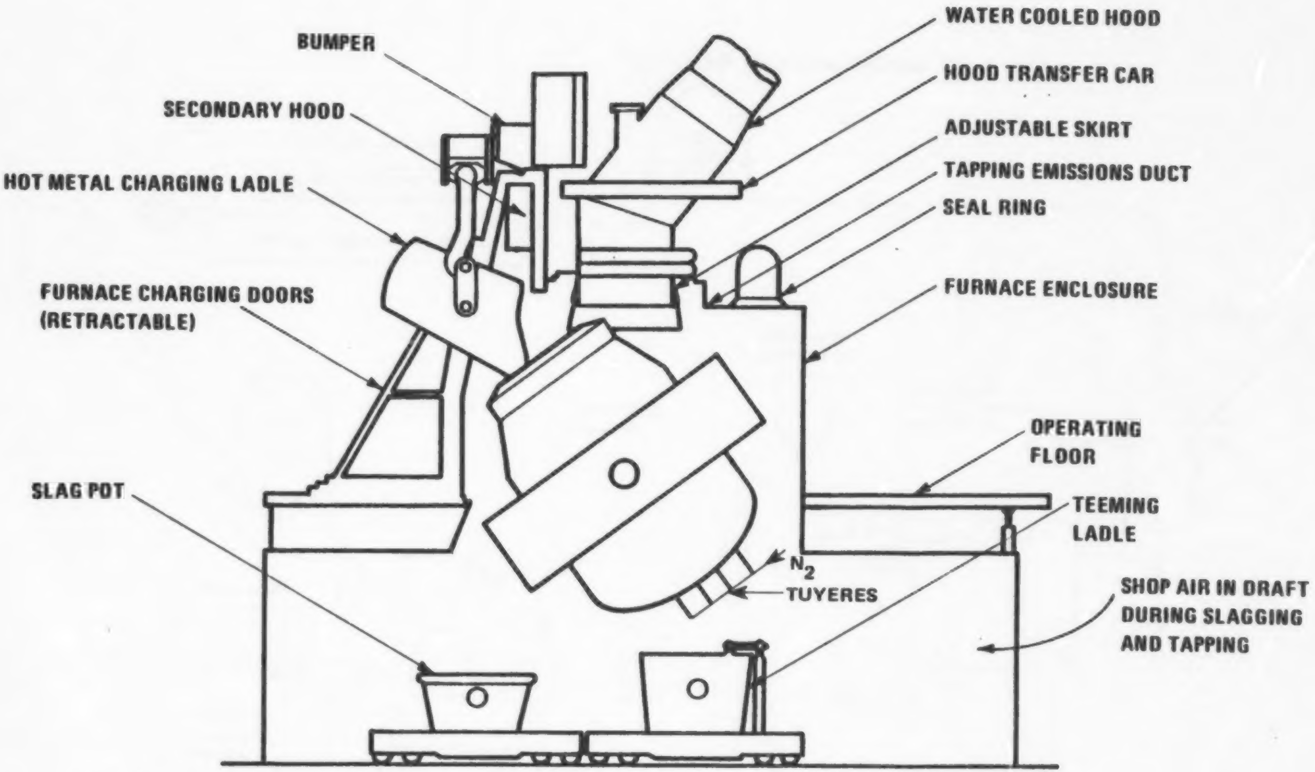

Figure 2. Schematic of Q-BOP vessel.

through the tuyeres to prevent their becoming plugged. The nitrogen flow rate is higher during hot metal charging than during scrap charging.

Shown in Figure 3 is a schematic of the fume control systems. The entire vessel and the fume collecting hoods are in an enclosure (referred to as a "doghouse"). The bottom side of the enclosure is open to allow tapping and slag dumping. All fumes generated during the oxygen blow are collected with the primary hood. When the vessel is tilted more than 20° (during charging, for example) the secondary hood collection system is automatically actuated and the primary system decreased to about 10 to 20 percent of full capacity (by damper adjustments). Design flow rates under this condition with both fans in operation is 10,600 m^3/min through the secondary hood system and 1,250 m^3/min through the primary system.

Testing was done on this furnace only during the periods that hot metal was being charged into the vessel. Two ladles of hot metal are charged for each heat. The average time of hot metal addition (2 ladles) during testing was 2.2 minutes. Sampling was in the secondary fume control duct just before the downcomer to the quencher (refer to Figure 3). Eight separate periods of hot metal addition (4 heats) were sampled in three hours. The overall sampling rate was near isokinetic (104 percent)--single point, no duct traverse. Gas volume collected was 1.027 dry standard cubic meters. Throughout this text the symbol Nm^3 is used to mean a cubic meter corrected to 20°C, 76.0 cm Hg, and 0% moisture.

Given in Table 1 are the pertinent process and sampling data. The scrap and hot metal figures are the sums for the four heats. Scrap is about 20 percent of the total metallics charged. The results obtained will be presented later.

BOF TESTING

The BOF shop in which the testing was conducted contains two vessels, each rated at about 250 tons/heat. Normally 6 to 8 heats can be completed on each vessel in an eight hour period. Shown in Figure 4 is a schematic of one of the vessels in the shop. Although this schematic is very similar to that for the Q-BOP, some important differences should be noted. First, and most important, there is no injection of gases (oxygen or nitrogen) through the vessel bottom. Thus, during scrap and hot metal charging, no gas (nitrogen) is blown into the metal. You will also note that secondary

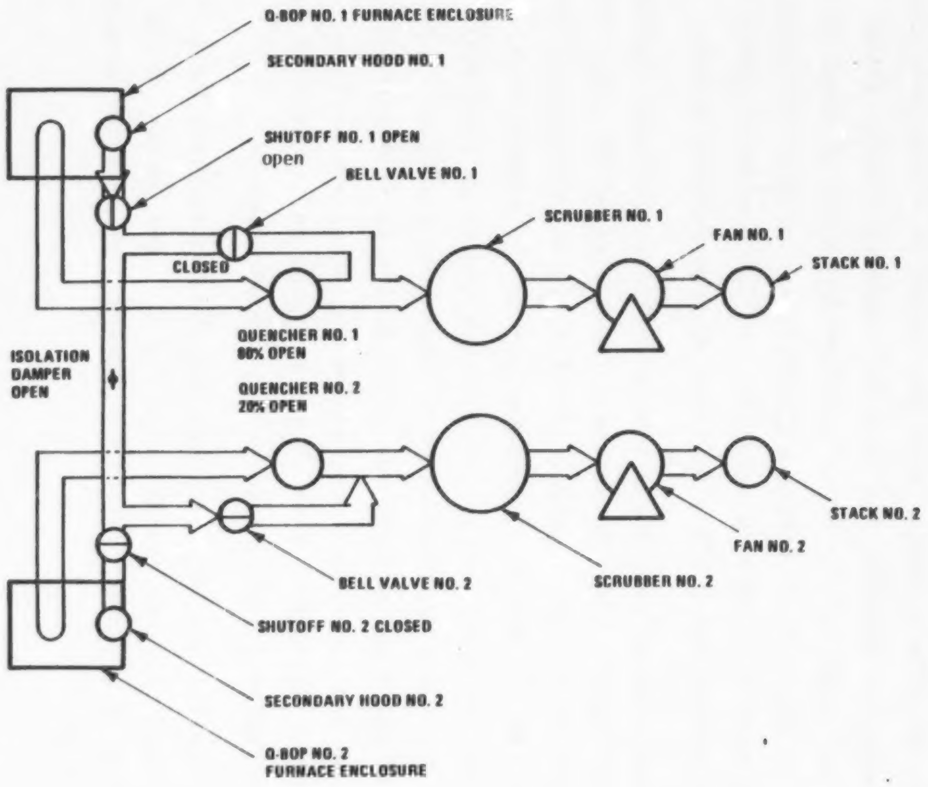

Figure 3. Gas collection system for Q-BOP.

TABLE 1. PROCESS AND SAMPLING DATA, Q-BOP

	Scrap, tons (Mg)	Hot Metal, tons (Mg)
Charging Data		
Total, 4 heats	206.5 (187.3)	822.7 (746.3)
Average/heat	51.6 (46.8)	205.7 (186.6)
Sampling Data		
Volume Gas Sampled		1.027 Nm^3
Stack Gas, Temperature		66.5°C
Stack Gas, Velocity		31.9 m/s
Stack Gas, Flow Rate		11,491 Nm^3/min
Sampling Rate, % Isokinetic		104

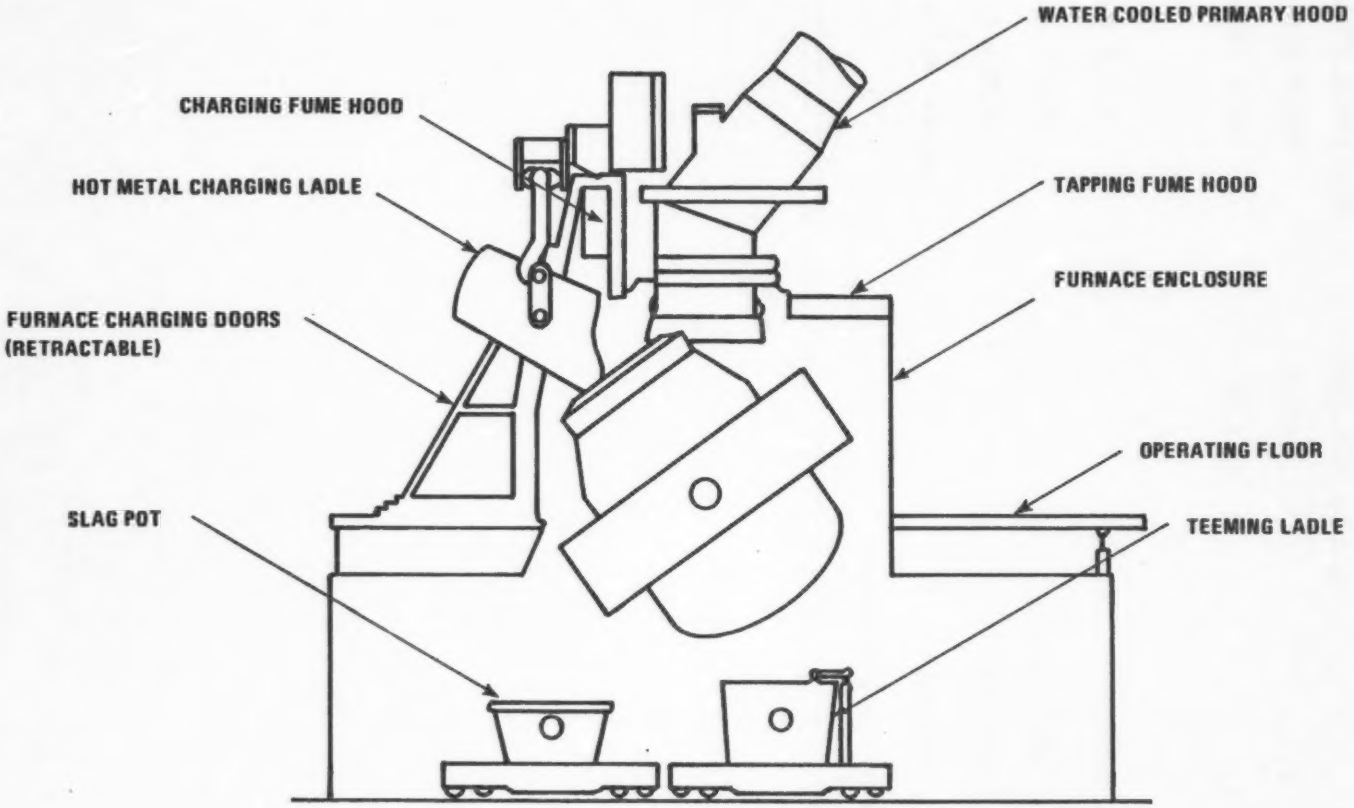

Figure 4. Schematic of BOF vessel.

fume collection hoods are on both the charging and on the tapping side of the enclosure.

Shown in Figure 5 is a schematic of the secondary fume collection system. Interlocks in the system prevent suction on the tapping hood or primary hood during the charging operations. Also, suction at the hot metal transfer and reladling station and on the charging fume hoods of the second vessel is prevented during charging the test vessel. During the tests, the second vessel was not in operation. Thus, only hot metal charging fumes were contained in the gas sampled.

Testing was conducted only during periods of hot metal charging. At this plant all hot metal needed for the heat is charged using only one ladle. Average time required for hot metal charging during the testing was 1.0 minutes. In order to obtain sufficient sample, sampling was carried out during 24 heats over a five day period. The sampling system was sealed between test periods. Only the second and third impinger solutions (which contain unstable reagents) were recovered each day. Therefore, data for individual heats are not available. Shown in Figure 5 is the sampling point for these tests. The overall sampling rate was 115.5 percent isokinetic. Total gas collected was 2.795 dry standard cubic meters.

Given in Table 2 are the pertinent process and sampling data. Both the total amount of scrap and hot metal charged for the 24 heats and the average amount per heat are given. The scrap charge for individual heats did not vary from the average by more than ± 19 percent. Hot metal charge for individual heats did not vary from the average by more than ± 7 percent. Scrap accounted for about 26 percent of total metallics charged.

For the sampling data, note that samples were taken from only one of the two charging fume collection ducts. The gas flow rate in each duct was measured and found to be essentially the same. Therefore, to calculate total flow rate and particulate mass, the results obtained were multipled by two.

DATA COMPARISONS

Particulates

In both tests the total particulate concentration in the gas was determined using the SASS train. The SASS train collects the particulate in four size fractions as given earlier. Additional particulate, probably containing

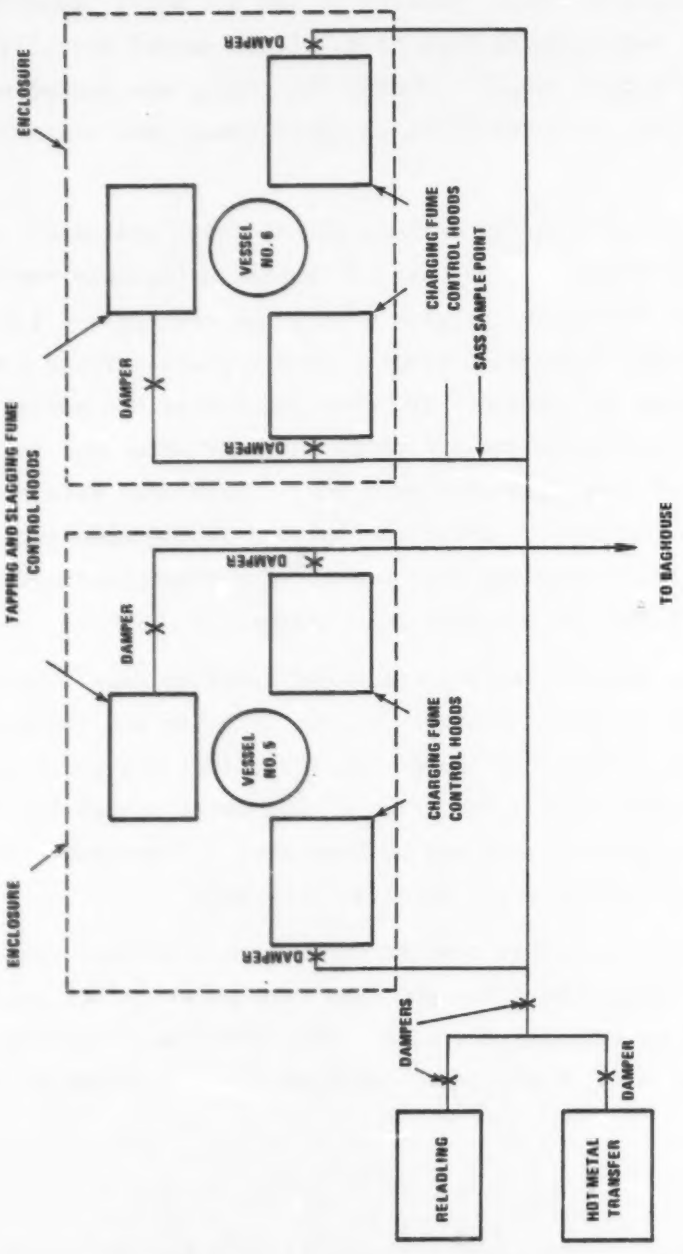

Figure 5. BOF shop secondary fume control system.

TABLE 2. PROCESS AND SAMPLING DATA, BOF

	Scrap, tons (Mg)	Hot Metal, tons (Mg)
Charging Data		
Total, 24 heats	1598 (1450)	4494 (4077)
Average/heat	66.6 (60.4)	187.2 (169.8)
Sampling Data		
Number of Heats Sampled		24
Gas Volume Sampled		2.795 Nm^3
Stack Gas, Temperature		85.3°C
Stack Gas, Velocity		26.5 m/s
Stack Gas, Flow Rate--Total Both Ducts		11,509 Nm^3/min
Sampling Rate, % Isokinetic		115.5

some of all size fractions, is trapped in the probe. Given in Table 3 are the total particulate and size fraction data.

The particulate concentration in the gas from the Q-BOP was substantially higher than from the BOF (1298 versus 788 mg/Nm^3). There is also a significant difference in the particulate size distribution. For the BOF, 27 percent of the particulate was less than 3 μm in size versus 16 percent of the Q-BOP particulate in this size range. About 70 percent of the Q-BOP particulate was larger than 10 μm whereas only 35 percent of the BOF particulate fell in this size range.

Shown in Table 4 is the mass of particulate generated in each size range per ton (or megagram) of hot metal charged. The important point to consider is that the Q-BOP appears to generate about three times as much particulate as does the BOF (per unit of mass of hot metal charged). Thus, about 17.6 kg of particulate is generated by the Q-BOP per 100 Mg of hot metal (35 lb/100 tons hot metal) versus about 5.3 kg of particulate per 100 Mg hot metal (10.6 lb/100 tons hot metal) generated by the BOF.

Inorganics

Given in Table 5 are the concentrations of a number of elements in the uncontrolled fume from the two vessels and the amount generated per megagram (1.1 tons) of hot metal added. There appears to be no substantial difference in the amounts of the elements contained in the fume. The calculations for the BOF are clouded somewhat since some of the analyses for individual SASS train components were reported only as MC (Major Components). For the BOF data, a > (greater than) symbol indicates that at least one of the SASS component samples was analyzed as a major component. MC indicates that the element was a major component in all SASS samples.

For the Q-BOP, nickel, iron, chromium, calcium, arsenic, lead, and possibly sulfur and phosphorous are at sufficiently high concentrations that the fume should not be emitted uncontrolled. For the BOF, the concentrations of barium, cadmium, selenium, arsenic, chromium, nickel, and possibly lead, calcium, and iron are sufficiently high that fume control is needed. Both plants tested do control the fume from hot metal charging. No testing was done on the outlet from the control device.

TABLE 3. PARTICULATE SIZE DATA FOR BOF AND Q-BOP

Size Range	BOF mg/Nm^3	%	Q-BOP mg/Nm^3	%
<1 μ	85	11	26	2
1-3 μ	124	16	182	14
3-10 μ	206	26	69	5
>10 μ	274	35	892	69
Probe, Cyclone Washes	99	12	129	10
Totals:	788	100	1298	100

TABLE 4. PARTICULATE MASS DATA FOR BOF AND Q-BOP*

	BOF		Q-BOP	
Size Range	lb/ton	kg/Mg	lb/ton	kg/Mg
<1 μm	11.6×10^{-3}	5.8×10^{-3}	7.0×10^{-3}	3.5×10^{-3}
1-3 μm	16.8×10^{-3}	8.4×10^{-3}	49.4×10^{-3}	24.7×10^{-3}
3-10 μm	28.0×10^{-3}	14.0×10^{-3}	18.6×10^{-3}	9.3×10^{-3}
>10 μm	37.0×10^{-3}	18.5×10^{-3}	242×10^{-3}	121×10^{-3}
Probe, Cyclone Washes	13.4×10^{-3}	6.7×10^{-3}	35.0×10^{-3}	17.5×10^{-3}
Totals:	10.6×10^{-2}	5.3×10^{-2}	35.2×10^{-2}	17.6×10^{-2}

*Calculated on the basis of hot metal added.

TABLE 5. SELECTED INORGANICS IN BOF AND Q-BOP FUME

Element	BOF		Q-BOP	
	Concentration In Gas+	Total Generated mg/Mg Hot Metal	Concentration In Gas+	Total Generated mg/Mg Hot Metal
Aluminum	MC		0.43	58
Antimony	0.006	0.4	<0.001	0.14
Arsenic	≤0.05	≤3.4	<0.02	<2.7
Barium	>0.11	>7.4	0.02	2.7
Bismuth	0.003	0.2	<0.0007	0.09
Cadmium	0.077	0.47	0.002	0.27
Calcium	MC		64	8671
Chromium	0.84	57	0.26	35
Copper	0.18	12	0.1	14
Iron	>2.7	>183	85.3	11,557
Lead	>0.02	>1.4	0.41	56
Magnesium	>0.55	>37	2.3	312
Manganese	>0.11	>7.4	3.8	515
Mercury	0.0008	0.05	>0.0031	0.42
Nickel	0.31	21	0.18	24
Phosphorous	MC		0.53	72
Selenium	0.087	5.9	<0.033	4.5
Silicon	>1.1	>74	4.2	569
Strontium	0.016	1.1	<0.056	7.6
Sulfur	>0.06	>4	7.9	1070
Zinc	MC		0.14	19

+Concentrations in mg/Nm^3.

Organics

Given in Table 6 are the total organics generated during hot metal charging of the BOF and Q-BOP. Note that the total organics generated per megagram of hot metal added is about 15 times higher for the Q-BOP than for the BOF. Also note that about 2/3 of the Q-BOP organic is adsorbed on the particulate matter but less than 10 percent of the organic from the BOF is adsorbed on the particulate.

Shown in Table 7 is a breakdown of this organic matter into the major organic compound categories. The major categories for BOF organics are aliphatic and aromatic hydrocarbons, and esters. Note that no evidence for fused aromatics--polynuclear--was found for the BOF. For the Q-BOP, the major categories are aliphatic hydrocarbons and fused (or polynuclear) aromatics. A variety of compound types are found in the Q-BOP organic.

A low resolution mass spectrographic analysis of the Q-BOP organic indicated the presence of organics with masses equivalent to the masses of known carcinogens. The sample was further analyzed by GC/MS. No carcinogenic organic compounds were found in this analysis.

CONCLUSION

In this paper a comparison has been made for the fumes generated during hot metal charging of a BOF and a Q-BOP. The data indicate that particulate generated in this operation is substantially greater for the Q-BOP than for the BOF. This is probably directly related to blowing gas into the bottom of the Q-BOP and through the metal charged. Data have been presented to show that there is not a significant difference in the types of inorganics in the fume.

The data also indicate that the fume from the Q-BOP contains substantially more, and significantly different types, of organic matter than fume from the BOF during hot metal charging. Although fume from the Q-BOP does contain polynuclear aromatic hydrocarbons, and none of these materials was found in fume from the BOF, no evidence of carcinogenic organic compounds was found.

TABLE 6. TOTAL ORGANICS IN BOF AND Q-BOP FUME

	BOF	Q-BOP
In SASS Particulates, mg/Nm^3	0.7	43.6
In SASS Organic Module, mg/Nm^3	7.9	20.5
Total Organic, mg/Nm^3	8.6	64.1
kg Organic/Mg Hot Metal	5.8×10^{-4}	8.7×10^{-3}
lb Organic/ton Hot Metal	11.6×10^{-4}	17.4×10^{-3}
kg Organic/heat	9.9×10^{-2}	1.62
lb Organic/heat	19.8×10^{-2}	3.24

TABLE 7. MAJOR ORGANIC COMPOUND CATEGORIES CONCENTRATIONS IN UNCONTROLLED FUME, mg/Nm^3

	BOF	Q-BOP
Aliphatic Hydrocarbons	0.3	7.7
Aromatic Hydrocarbons	0.2	1.4
Fused Aromatics	0	4.9
Alcohols	0	2.6
Amines	0	1.3
Amides	0	1.3
Esters	0.9	2.6
Carboxylic Acids	0	3.0

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FIELD EVALUATION OF FUGITIVE EMISSIONS FROM BOF STEELMAKING SHOPS

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ABSTRACT

This paper presents the findings of week-long field evaluations of emission controls of six (6) BOF steelmaking shops. The field evaluations included shops with complete furnace enclosure, Gaw damper plates, and tap-side enclosures. For each evaluation, process engineers stationed inside the furnace control room and on the operating floor carefully documented process operations. Simultaneous with in-shop process evaluation, outside observers recorded visible emissions from the shop roof monitors in accordance with EPA Method 9. FM radio contact between in-shop and outside observers enabled documentation of the source of all roof monitor emissions. Performance of each control system is presented on the basis of average roof monitor opacity for each furnace operation, i.e., charge, oxygen blow, tap, etc. Also investigated were the potential causes of roof monitor emissions such as variations in steelmaking procedures and/or emission control operational variables.

FIELD EVALUATIONS OF FUGITIVE EMISSIONS FROM BOF STEELMAKING SHOPS

INTRODUCTION

GCA is conducting field evaluations of secondary emission controls at BOF shops for EPA Region V. The primary objective is to document the opacity of roof monitor visible emissions (RMVE) for each vessel operation; i.e., scrap charge, hot metal charge (HMC), oxygen blow and reblow, turndowns and tapping. A secondary objective is to evaluate all process data that describes how the vessels and the emission control systems were operated in order to achieve the performance levels observed. This second objective has become an important aspect of the program since operational practice has such a strong impact on emissions that escape capture and are emitted from shop roof monitors.

This paper summarizes the highlights of six (6) BOF studies conducted between June 1979 and August 1980. When reviewing these data, the reader should recognize that the control system and emissions data describe the system performance observed by GCA during the week(s) of testing. The final reports prepared for each field test contain a complete record of steelmaking process variables and emission control operation during testing. Evaluations of other BOF shops are currently in progress.

DATA COLLECTION AND ANALYSIS METHODOLOGY

Field evaluations are conducted by GCA engineers familiar with BOF shop operations. Each team member is certified to observe visible emissions (VEs) in accordance with EPA Method 9. RMVEs are continuously recorded by outside observers while inshop observers document shop operations. Continuous FM radio contact between all observers enables determination of the origin of each RMVE. This approach is discussed further below.

Visible Emissions Observations

VE data are collected in accordance with EPA Reference Method 9 as published in the Federal Register, 40 CFR Part 60.275, Appendix A. Ground level positions are normally used to evaluate emissions against the sky. Occasionally, RMVE are blown horizontally across the length of a shop roof monitor. As directed by Method 9, these emissions are observed against the best available contrasting background which is usually the roof monitor area. Normally, however, VE observers are able to view emissions at a point just above the roof monitor. This approach avoids the possibility of inaccurate measurements in the event the plume travels horizontally for a brief period before rising upwards. The densest portion of the plume is observed, as specified in Method 9.

Constant FM radio contact enables precise documentation of which shop operation caused each visible emission. By receiving instant radio confirmation of what process is occurring, VE observers know when emissions of no interest occur; i.e., hot metal transfer, skimming, and teeming.

Inshop Process Observations

Process observers are stationed at strategic locations within the shop to allow observation of all emission-causing operations. An engineer is assigned to each operating furnace to record process data and the precise time each operation occurs - scrap charge, HMC, oxygen blow, turndowns, etc. This observer closely monitors the control room instrumentation and documents the steelmaking techniques in use. He also observes each vessel operation from the working floor and estimates the approximate magnitude of emissions that escape capture. Constant radio contact with outside VE observers enables determination of the origin of each RMVE. Process data collected in the control room generally consists of: oxygen blow rates and net quantity blown, lance height, at each interval, tons of steel and scrap charged, hot metal (and tap) temperature and chemistry, time of flux additions, etc.

Emissions escaping capture at the furnace are evaluated by one of two techniques. When the uncontrolled emission can be observed, a percent capture is estimated. If the total uncontrolled emission is not visible, the observer records the magnitude of emissions escaping capture by the following criteria: light, 5 to 25 percent opacity, (as viewed within the shop); moderate, 30 to 60 percent opacity; and heavy, 65 to 100 percent opacity. Also recorded are the duration of each vessel operation and any unusual operating practices.

When necessary, another process engineer records process data at the gas cleaning device, to document control system operation and the exhaust flow rate applied to the furnaces. Often, these data are available in the BOF control room, or continuously recorded at the gas cleaning device. .

In some shops, observer(s) are required to document the precise time of non-furnace operations such as teeming, hot metal transfer, or skimming. Often, emissions from these operations can be observed by one of the furnace observers.

Data Handling and Assessment

After each day, observers review their data sheets for clarity and consistency. The Lead Engineer collects all data and reviews them once again. VE data sheets are handled by the chain-of-custody technique and kept in a secure area at GCA until the final reports are submitted to EPA.

In the office, the average opacity for each vessel operation is calculated. If requested, compliance with the applicable opacity standard is also determined. When multiple shop or furnace operations occurred, the corresponding VE observations are not included in the summary tables. Only the RMVE whose origin can be absolutely determined by the radio communication technique are used to compile the data presented in this paper.

BOF SHOP AND EMISSION CONTROL SYSTEM DESCRIPTIONS

The six (6) BOF shops and their control systems are briefly described below. Additional data is available in the GCA report for each shop and also in the open literature.

Republic Steel, South Chicago, Illinois

The two 204-m ton* (225-ton) Q-BOP furnaces at RSC/Chicago replaced four 204-m ton (225-ton) open hearth furnaces in 1977 and operate within the old open hearth shop. The eight Q-BOPs currently operating in the U.S. represent more than half the number of basic oxygen process furnaces entering service in the last 7 years. The six other Q-BOPs are operated by US Steel, three apiece at Fairfield and Gary.

The Q-BOP differs from the conventional BOF in that instead of top blowing oxygen through a water-cooled retractable lance, oxygen and fluxes are blown through the bath via tuyeres in the furnace bottom. Because the vessel is bottom blown, the Q-BOP has some unique emission control problems when compared to a conventional BOF.

Primary emissions generated during the oxygen blow are captured by a retractable water-cooled skirt that is lowered over the mouth of the furnace, acting as a conventional, suppressed combustion hood. Furnace off-gases are cooled to 1093°C (2000°F) in water-cooled ductwork before entering the quenchers. The quenchers consist of two parallel venturis followed by impact separators that cool the gas stream to 80°C (175°F). Cooled gases pass through the venturi scrubbers which operate at a pressure drop of 150 mm Hg (80 in. W.C.) during the oxygen blow. Particulate entrained in the water droplets exit the venturi section and enter a fixed vane separator before the exhaust passes through the induced draft (ID) fan and stack.

At RSC, only one furnace is normally on-line since the enclosure system is designed so the fan on the down furnace supplements the operating furnace's fan for more draft during charging and tapping. Captured secondary emissions are exhausted to two venturi scrubber systems that operate in parallel. However, the quenchers are bypassed since the secondary exhaust stream is much cooler than the primary exhaust.

All secondary emissions are captured through a charge side hood located inside the enclosure. During scrap and hot metal charges, the enclosure door opening is minimized, and an exhaust flow rate of about 170 m^3/sec (360,000 acfm) is provided to the charge-side hood by both fans. During a tap, the charge-side doors remain closed, and the charge-side hood operates at 170 m^3/sec (360,000 acfm). Total exhaust is reduced to about 144 m^3/sec (305,000 acfm), during turndowns for sampling. During idle periods; i.e., waiting for the chemistry analysis, the system operates at about 106 m^3/sec (225,000 acfm).

Republic Steel, Gadsden, Alabama

Primary emissions generated during the oxygen blow are captured by a water-cooled, full combustion hood located 0.75 m (2-½ ft) above the vessel mouth. Before entering the ESP, furnace exhaust gases are cooled by a cascade-type evaporative chamber which also improves particle resistivity for better collection. Full system draft of approximately 30 mm Hg (283 m^3/sec or 600,000 acfm measured at the stack) is used during the HMC and oxygen blow. Partial draft of approximately 18.7 mm Hg (165 m^3/sec or 350,000 acfm measured at the stack) is used during scrap charging, turndowns, tapping, and slagging. Lance hole covers were present on one vessel during GCA's evaluation.

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*Metric ton.

The Gaw damper (closure plate) is a water-cooled steel plate which slides in a horizontal plane across the opening of the primary hood. The damper reduces the hood opening and increases the capture velocity of the primary exhaust system. The Gaw damper was designed to close off 75 to 80 percent of the hood opening during the HMC according to design data. The damper is designed for a furnace tilt angle not exceeding 45 degrees from vertical.

The first Gaw damper was retrofit to the No. 1 vessel in June 1977 at a cost of $350,000 according to RSC. The leading edge of the plate warped badly after 6 to 9 months of operation, and water cooling was installed on this edge of the plate. The maintenance cost of the water system proved less than the replacement cost of the plate, and a similar, water-cooled Gaw damper was installed on the No. 2 vessel in November 1978 at a reported cost of $425,000.

During tapping, the rotation of the vessel places the mouth of the furnace a considerable distance from the hood opening. To help contain tapping emissions and divert them into the primary hood, a tap-side enclosure was constructed on each furnace. The Gaw damper is not used for tapping emissions control because the necessary I-beam supports would interfere with charging at the other side of the furnace.

U.S. Steel, Gary No. 1 BOF

This shop is an open hearth conversion and the three 195-m ton (215-ton) vessels entered service in 1965. Annual production capacity of carbon and alloy steels is 4.0 MM m tons (4.4 million tons) for the three vessels combined.

U.S. Steel considers this shop a "one-and-a-half" vessel operation. Normally, two furnaces are available for steel production, with the third either on standby or down for reline. One vessel normally operates at maximum production to supply the continuous caster, producing 9 to 10 heats per 8-hour turn. The second vessel usually operates in a manner not interfering with the principal vessel, and produces 5 to 10 heats per turn. Normal shop production is 51 heats per 24-hour period.

Primary emissions are collected by conventional water-cooled, full combustion hoods at each of the three vessels. Each hood discharges into a common exhaust manifold that leads to the scrubber system. Isolation dampers close off the off-line furnace(s).

The gas cleaning system consists of two identical scrubbers operating in parallel. Furnace exhausts pass through a variable throat venturi, through a flooded elbow, and into a separation tower. Exiting the tower, gases pass through a 4100 kW (5500 hp) fan (at -103 to -150 mm Hg or -55 to -80 in. W.G. static pressure) and into a final separator.

The emission control system was designed for two furnaces on oxygen blow and one furnace on HMC, with a total exhaust flow of 307 m^3/sec (650,000 scfm), sat. Induced draft fans operate in three distinct modes, drawing 1800, 2400 or 3800 kVa (each). Fan load is mainly controlled by upstream louvers which operate at 50, 80, and 100 percent open for the three modes. Fan loads are also a function of the automatic control of the variable throat venturis.

Exhaust flow rates applied to each furnace depend on the isolation damper position, the fan load and venturi pressure drop, and the number of furnaces on-line. The flow rates at each furnace are measured in terms of static pressure in the quench section and recorded on continuous strip charts. The isolation damper set points are 20 percent open for scrap charging, turndowns and tapping, and 100 percent open for HMC and oxygen blows.

The Gaw dampers at Gary were designed to close off 70 percent of the hood opening during HMCs, according to design data. The damper is not used for scrap charging control because of possible damage from large scrap pieces, and because the furnace mouth is tilted too far away from the exhaust hood.

Furnace tilt during HMC is limited to 35° from vertical. Charging ladle spout extensions enable positioning of the ladle well into the furnace, bringing the point of emissions closer to the primary hood. Sheet metal curtain walls constructed above the furnace and Gaw damper, on the charge side, help minimize adverse effects of cross-drafts. The crane operator has instructions to slow or stop pouring should HMC emissions escape capture.

Total installed cost of the three Gaw damper systems in late 1978 and early 1979 was $750,000 according to U.S. Steel engineers. To date, there have been no major operation or maintenance problems with the dampers. The plates are constructed of one-quarter inch carbon steel and have not become warped. Only the rails supporting the wheels upon which the plate rides into position are water-cooled. The original wheel design had to be modified to avoid binding from build-up of dusts in the rails. The damper is installed 6-inches below the primary exhaust hood because of the proximity of a major structural beam.

To help contain tap fumes and direct them into the primary exhaust hood, a tap-side enclosure was installed in 1977 on each furnace. The furnace isolation damper is automatically set at 20 percent open during tapping. The Gaw damper is not used. No significant maintenance or operational problems exist with the current enclosures according to U.S. Steel engineers.

National Steel, Great Lakes Steel Division

Primary emissions generated during the oxygen blow are captured by full combustion hoods located directly over each furnace mouth. Air is pumped into the hood system, approximately 0.33 m (10 feet) above the hood mouth, at a rate of 28.3 m^3/sec (60,000 scfm) to help combust carbon monoxide. Temperature activated water sprays in the exhaust hood ducting control moisture and temperature. The oxygen lance opening in the primary exhaust hood is fitted with a sliding disk seal to reduce the escape of emissions and loss of draft.

To help contain tapping emissions, doors (referred to as garage doors) were installed on the tap-side of the furnace. The doors retain tap emissions long enough to allow fumes to be carried into the primary exhaust hood.

Inland Steel, No. 4 BOF Shop

Inland Steel operates two basic oxygen furnace (BOF) shops at the Indiana Harbor Works. Two 231-m ton (255-ton) top blown furnaces at the No. 4 shop entered service in July 1966, and presently have an annual rated capacity exceeding 3.6 million m tons (4.0 million tons) of steel.

Primary emissions generated during the oxygen blow are captured by a full combustion-type hood over each furnace. No secondary emission controls are present for charging, turndowns, tapping, or slagging. Steam rings located on the circumference of the lance holes above each combustion hood, help to control the escape of oxygen blow emissions.

Furnace exhaust passes from the primary exhaust hood through the spark box for water spray cooling, and into a quench tower. The gas stream is then spilt into four identical Buell venturi scrubbers operating in parallel. Water laden gas enters a moisture separator prior to the four parallel, 1300 kW (1750 hp) ID fans. The four streams are combined and discharged through a single stack.

The emissions control system is designed to operate with one furnace on oxygen blow. Guillotine dampers isolate the off-line vessel. According to stack tests performed in 1974, the exhaust flow through the scrubbers is 229 m^3/sec (484,500 acfm), at 58°C (128°F).

Ford Steel Division BOF Shop, River Rouge Plant

The two 227-m ton (250-ton) top blown BOFs, installed in 1964, have combined annual production capacity of 2.7 million m tons (3 million tons) per year. The shop produces primarily low carbon sheet for use in automobile manufacturing.

The scrap charge, composed of home and purchased scrap, is predominantly clean No. 1 bundles from nearby auto stamping facilities. The two BOFs employ a three-holed lance with an oxygen blow rate of 10.4 m^3/sec (22,000 scfm).

Primary emissions are captured by a full combustion, water-cooled hood. Exhaust gases are cooled in a cascade-type evaporative chamber prior to entering an ESP. Steam injection at the evaporator chamber improves particle resistivity. An isolation damper regulates exhaust rates during various furnace operations. The ESP is equipped with four fans, dividing the gas flow among eight ESP banks with four fields per bank. The pressure drop measured across all compartments is about 5.6 mm Hg (3 in. W.C.).

Secondary emissions during HMC are controlled by Gaw damper plates installed in 1973. GCA observed the plate to close off approximately 50 percent of the primary hood opening. The vessel is tilted 30° from vertical at the beginning of the HMC and lowered to 45° from vertical at the end of the HMC. Since GCA's evaluation, Ford has removed the Gaw damper and is experimenting with a modified doghouse enclosure to control secondary emissions.

ANALYSIS OF FUGITIVE EMISSIONS FROM BOF SHOP OPERATIONS

The following section characterizes the performance of six BOF secondary emissions control system relative to the following BOF process operations:

- Scrap Charge (SC)
- Hot Metal Charge (HMC)
- Oxygen Blow (O_2 Blow)
- Turn Down (TD)
- Tapping
- Slagging

Note that the findings presented herein are based on detailed analyses of process information available for six BOF studies. In some cases, the analyses are somewhat limited by the extent of process data supplied to GCA, and monetary constraints imposed by each project.

For comparison of RMVEs between shops, the authors employed an analysis tool termed the opacity-duration product. The opacity-duration product is defined as the product of: (1) the percentage (in fractional form) of operations showing RMVEs greater than zero percent opacity; times (2) the average opacity of RMVEs greater than zero; times (3) the average duration of those RMVEs. The opacity-duration product essentially represents an average visible emissions flux for each furnace operation.

Scrap Charge

Each heat begins with the addition of cold scrap to the empty vessel. Many of the shops evaluated were equipped with hydraulic (Calderon type) scrap charging systems although only GLS and Inland regularly used their systems. RSC/Gadsden and GLS employed two scrap charges while the other shops charged scrap in a single operation.

RMVEs from scrap charging represented a relatively small portion of BOF secondary emissions in these shops. SC emissions resulted from ignition of oily material and other combustibles as the scrap contacts the hot vessel. Control of SC emissions was minimal at the shops evaluated except at the RSC/Q-BOP where SC emissions are captured by the secondary hood within the enclosure. At most of the BOF shops, primary exhaust drafts were dampered off to between 10 to 30 percent open, during the SC. Gaw Dampers are not designed to control SC emissions since they are not effective in controlling scrap charge emissions. Also dampers could be damaged by large pieces of scrap.

Table 1 summarizes the RMVE data collected (for SC) at the six BOF shops. GLS/Ecorse and the RSC/Q-BOP showed the lowest RMVEs for scrap charging. Note that while the estimated capture of SC emissions at the RSC/Q-BOP was 90 percent, GLS/Ecorse showed zero RMVEs with reduced hood capture of about 50 percent. The data indicate that other factors such as scrap composition and quality can play an important role in reducing SC emissions.

Five process parameters typically evaluated for their relationship with scrap charge RMVEs were: (1) scrap composition and quality; (2) scrap quantity; (3) duration of scrap charge; (4) quantity of slag in vessel; and (5) temperature of vessel.

TABLE 1. SUMMARY OF SCRAP CHARGE DATA FOR SIX BOF SHOPS

BOF shop	SC emission control	Uncontrolled magnitude[a]	Estimated capture	Percent of scrap charges showing RMVE > 0 (%)	Average opacity of RMVEs > 0	Average duration of RMVEs > 0	Peak RMVEs (% opacity)	Opacity-duration product[b] (% opacity-seconds)	Comments
RSC/Chicago Q-BOP	Doghouse enclosure w/local hood	Light	90	18	6	15	10	17	Very clean scrap, minimal fines, mostly ingots, butts and reclaim. Dolomite sprayed on scrap prior to charging.
RSC/Gadsden (Avg. of 2 vessels)	None	Moderate to heavy	50	48	8	62	40	230	Two scrap charges by transfer crane. Home scrap and No. 1 and No. 2 purchased scrap charged.
USSC/Gary No. 1 BOF (Avg. of 3 vessels)	None	Light	10	11	15	50	40	83	Vessel isolation dampers closed to 20% open during SC. 60 to 70% clean scrap, ~10% bundles, 12% pit, ~12% misc. Generally low oil, clean scrap.
Inland Steel No. 4 BOF	None	Moderate	0-10	13	5.0	45	5.0	29	Medium quality scrap, few bundles, some oil in scrap.
GLS/Ecorse No. 2 BOF	None	V. light	~50	0	0	0	0	0	Two scrap charges, clean bundled scrap, probably stampings from auto mfg. Mostly purchased scrap.
Ford Steel	None	Light	~50	20	14	95	50	270	Clean bundled scrap, probably stampings from auto mfg. Home and purchased scrap.

[a] Light = 5 to 25 percent opacity for emissions escaping the vessel, observed inside the shop.
Moderate = 30 to 60 percent opacity for emissions escaping the vessel, observed inside.
Heavy = greater than 60 percent opacity for emissions escaping the vessel, observed inside.

[b] Product = portion of SC showing emissions x average opacity x average duration of emissions.

At one shop, correlations between scrap composition and RMVEs from scrap charging were reflected in the data as shown in Table 2. Generally, clean home scrap (Grade 1) from the Gadsden mills generated somewhat lower RMVEs compared to purchased scrap (No. 2 heavy melt, consisting of recycled machinery).

TABLE 2. SCRAP COMPOSITION AND EMISSIONS GENERATED DURING SCRAP CHARGING AT RSC/GADSDEN BOF SHOP

Scrap type	Scrap composition	RMVEs[a] range of (% opacity)
Home Scrap		
Clean home scrap	Blooming mill scrap Rotary shear scrap Teeming mold scrap	0 to 5
Medium grade scrap	Strip mill scrap	0 to 5
Galvanized scrap	Galvanized sheet metal	5 to 10
Reclaim	Iron bearing BOF slag	0 to 35
Purchased Scrap		
No. 1 heavy melt	Recycled machinery (clean)	0 to 5
No. 2 heavy melt	Recycled machinery (low quality, with oil)	5 to 40

[a] For all heats, both vessels, measured at BOF shop roof monitor.

At RSC/Gadsden, strip mill scrap appeared to contain the greatest amount of oil, while blooming mill scrap (low oil content), charged alone, generated almost no emissions. Charging of galvanized metal generated white zinc oxide RMVE ranging from 5 to 10 percent opacity. Reclaim, a low quality scrap, often generated fine-sized particulate emissions during charging. Emissions from purchased scrap (No. 1 and No. 2 heavy melt) are attributable to foreign, nonferrous material present in the scrap.

Hot Metal Charging

In all shops evaluated, hot metal is charged to the vessel by overhead cranes. The slowest HMC rate was 63.6 m tons/min (70 tons/min) at RSC/Gadsden while the highest was 319 m tons/min (351 tons/min) at GLS/Ecorse. At the RSC/Chicago Q-BOP, two HMCs were required per heat because of the small shop ladle size (91 m ton). All other shops used one HMC per heat. Furnace tilt angles ranged from 30° to 45° from vertical. In most cases, cranemen tried to keep the charging ladle as close as possible inside the vessel mouth.

In many shops, RMVEs from HMCs represent a major portion of emissions from BOF process operations. As shown in Table 3, four of the shops showed RMVEs in the moderate to heavy range (roughly 50 to 70 percent opacity, observed inside the shop) while two of the shops generated very heavy HMC emissions (always 100 percent opacity as seen inside the shop). These differences in uncontrolled emissions may be due to scrap quality and hot metal charge rates, as discussed later.

HMC controls assessed included two shops with no controls, three shops with retrofit Gaw dampers, and one shop with an enclosed and secondary hood. Republic Steel's Gadsden BOF and the Chicago Q-BOP, which employed substantially higher evacuation rates, showed the best capture of HMC emissions. USSC/Gary's No. 1 BOF, employing a lower design HMC evacuation rate (GCA engineers believe that actual rates were much higher) showed generally lower HMC emissions capture. However, capture did vary at Gary, generally increasing as the number of vessels on-line decreased. HMC evacuation rates at the remaining shops were not available, but were thought to be lower as reflected by in-shop observations. GCA observers noted that the evacuation system at Inland appeared to be inoperative during HMC's. (Recall that there were no secondary controls at Inland's No. 4 BOF shop.)

A comparison of RMVE data in Table 3 clearly shows that the Republic Steel Chicago Q-BOP and Gadsden BOF produced the lowest RMVE during HMC of all the shops evaluated. The USSC/Gary No. 1 BOF also showed relatively low HMC emissions, while the Ford BOF and the two uncontrolled shops showed substantially higher emissions. Note that at RSC/Gadsden and USSC/Gary, exhaust drafts may have been increased to improve HMC capture (these steps may have reduced gas cleaning efficiency). The other shops operated exhaust flows under standard procedures. The RMVE analysis suggest that properly designed and operated retrofit Gaw dampers can approach the degree of HMC emissions control provided by a secondary hood and enclosure.

The following process variables which might effect HMC emissions were evaluated: (1) scrap quality; (2) ladle handling and positioning; (3) hot metal charge rate; (4) hot metal temperature and chemistry; and (5) hot metal/scrap charge ratio. In general, the minimal variations of these process parameters within a single shop did not provide adequate data to show any substantial correlations with RMVEs. Also, the masking effect of other process variations further complicated the analyses. A data base on the order of 100 heats per operating vessel would likely be required to conduct an in-depth evaluation employing multiple regression analysis techniques.

General trends noted at RSC/Gadsden indicated that low quality reclaim, No. 2 heavy melt, and medium quality strip mill scrap produced the highest HMC emissions at that shop. High quality home scrap (blooming mill scrap and ingots) showed no RMVEs during HMC. The above trends were exactly reversed for data collected at USSC/Gary. Similar contradictions were noted for shop ladle handling practices. At Gadsden, nine cases of poor ladle handling resulted in only one case of RMVEs greater than 0. However, at USSC/Gary, where HMC emissions abatement procedures required attenuation of the HMC pour rate when emissions were heavy, in-shop observers noted decreased emissions when ladles were carefully poured.

TABLE 3. SUMMARY OF HOT METAL CHARGE (HMC) DATA FOR SIX BOF SHOPS

BOF shop	Secondary emission control	Uncontrolled emissions magnitude[a]	Estimated capture (%)	Control system evacuation rate m^3/sec (dscfm)	Percent of HMCs showing RMVE >0 (%)	Average opacity of RMVE >0 (% opacity)	Average duration of RMVEs >0 (seconds)	Peak RMVEs (% opacity)
RSC/Chicago Q-BOP	Doghouse enclosure w/local hood	Moderate	90	156 (330,900)[b]	57	8	42	25
RSC/Gadsden BOF	Gaw damper	Moderate	80	230 (490,000)[c]	59	7	54	30
USSC/Gary No. 1 BOF	Gaw damper	Moderate to heavy	40-100	44 (94,000)[d]	53	15	81	75
Inland Steel No. 4 BOF	None	Moderate to heavy	0-10	-0[e]	90	34	112	90
GLS/Ecorse No. 2 BOF	None	Very heavy	-30-40	NA[f]	100	53	132	100
Ford Steel BOF	Gaw damper[g]	Very heavy	-30-40	NA[f]	100	31	143	95

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[a] Light = 5 to 25 percent opacity for emissions escaping the vessel, observed inside the shop.
Moderate = 30 to 60 percent opacity for emissions escaping the vessel, observed inside the shop.
Heavy = greater than 60 percent opacity for emissions escaping the vessel, observed inside the shop.

[b] Measured during stack tests.

[c] From data collected at shop.

[d] Flow rate provided by USSC design drawings, generally thought to be higher as observed by GCA.

[e] Control system appeared inoperative.

[f] Not available.

[g] A representative from Ford indicated that the Gaw Damper system at Ford has been removed in order to experiment with "Dog House" enclosures for collection of secondary emissions.

Evaluation of HMC pour rates for individual BOF shops showed no substantial correlations with RMVEs. However, a collective evaluation of HMC data for all six BOF shops, presented in Table 4, clearly shows that shops employing higher HMC pour rates produced substantially greater RMVEs. Note that the masking effect of process variations is minimized in Table 4 because the data base represents over 200 heats of data. Deviations from the general trend are attributable to differences in secondary emissions controls at each shop.

TABLE 4. COMPARISON OF HMC POUR RATES AND RMVEs

Shop	Secondary emissions control	HMC pour rate (t/min)[b]	(1) Percent of HMCs showing RMVEs >0	(2) Average opacity of RMVEs >0 (%)	(3) Duration of RMVEs >0 (seconds)	Opacity-duration product[a]
RSC/Chicago	Secondary hood	92	57	8	42	190
RSC/Gadsden	Gaw damper	70	59	7	54	220
USSC/Gary	Gaw damper	190	53	15	81	640
Inland	None	184	90	34	112	3400
Ford	Gaw damper	216	100	31	143	4400
GLS	None	351	100	53	132	7000

[a] Product of columns labeled (1) (2) and (3) showing relative magnitude of RMVEs.

[b] m tons/min can be obtained by multiplying t/min by 0.908.

Oxygen Blow

The basic oxygen process converts a charge of molten iron and scrap to steel by blowing large quantities of oxygen through the charge. The oxidation process lowers carbon and silicon content and provides heat for melting the scrap. Supplementary fuel sources such as silicon carbide were added to the vessel in some of the six shops. Oxygen blow rates ranged from 15,000 to 24,000 scfm at the six shops evaluated. Hot metal to scrap charge ratios ranged from 1.8 to 3.6. Oxygen blows at the BOF shops evaluated ranged from 13 to 22 minutes in duration. For the top blown vessels, fluxes are charged through overhead chutes after ignition of the off gases has been achieved. Fluxes are charged to the Q-BOP through the center tuyeres.

Origin of RMVE During Oxygen Blows. At many BOF shops, oxygen blow emissions are a major contributor to RMVEs. The heaviest RMVEs generally occur towards the middle of the oxygen blow (approximately 12 to 13 minutes into the blow) when a critical period is reached as the scrap becomes suspended in the bath and melts completely. During this period, the scrap overturns and the bath erupts violently, occasionally splashing hot metal from the vessel. At this point, carbon and silicon are oxidized at the greatest rate, increasing fume generation and the potential of fume escape from primary hoods.

RMVEs from the oxygen blow at the top blown BOF shops originated from three main sources; (1) leakage from cracks and expansion gaps in the primary hood and exhaust ductwork; (2) leakage from the lance hole in the primary hood; (3) fumes escaping capture at the vessel mouth.

The five top blown BOF shops employed open, full combustion primary hoods. The vessels at three of the top blown BOF shops were fitted with lance hole covers or steam rings at the lance hole to contain oxygen blow emissions. On vessels with lance hole emission control, emissions from the lance hole area were significantly reduced. The reduction of oxygen blow RMVEs through the use of lance hole covers is illustrated in Table 5 which shows RMVEs from Vessel 1 (no lance hole cover) and Vessel 2 (with lance hole cover) at RSC/Gadsden.

Oxygen blow emissions originating from cracks and gaps in the primary hood and ductwork are largely related to the level of maintenance of the primary emission control system at each shop. This point is illustrated in Table 5 by comparing oxygen blow RMVEs from Inland's No. 4 shop to RMVEs from other shops evaluated. In-shop engineers noted that lance hole emissions were minimal, due to the steam ring controls, but holes and gaps in the primary control system ductwork were responsible for most of the RMVEs at Inland. Conversely, the doghouse enclosure and ducting at the Q-BOP showed no signs of leaks, and RMVE were 0 for all oxygen blows. Oxygen blow RMVEs from the other top blown BOF shops, where primary exhaust ducting was better maintained, were significantly reduced.

Primary Emissions Control of Oxygen Blow Emissions. Data presented in Table 5 shows that the Q-BOP with suppressed combustion and wet scrubber emission controls showed the lowest oxygen blow RMVEs (0 opacity) of all shops evaluated. The Q-BOP also employed the lowest control system exhaust rates (primary and secondary combined) in part due to the use of suppressed combustion system. The remaining top-blown shops all employed full combustion hoods with either ESP or wet scrubber controls. Lack of correlation between oxygen blow RMVEs and control system exhaust rates is likely due to the effect of quencher and scrubber spray additions which effect the actual exhaust rate at the hood. However, Ford's BOF shop, which produced the lowest oxygen blow RMVEs among the top-blown shops, employed the highest exhaust rate per operating vessel of all top-blown shops.

TABLE 5. SUMMARY OF OXYGEN BLOW DATA FOR SIX BOF SHOPS

BOF shop and vessel I.D.	Emissions control system	Control system evacuation rate m^3/sec (acfm)	Oxygen blowrate m^3/sec (scfm)	Hot metal to scrap charge ratio	Percent of heats showing RMVE > 0% (%)	Average opacity of RMVEs > 0 (% opacity)	Average duration of RMVEs > 0 (seconds)	Peak RMVEs (% opacity)	Opacity-duration product[a] (% opacity-seconds)	Comments
RSC/CHICAGO Q-BOP 2 Vessels	Doghouse enclosure, suppressed combustion, plus secondary hood to wet scrubbers	59^b (125,000) plus 56.6^b (120,000)	10.6 (22,500)	3.6	0	0	0	0	0	Vessel lining thin, frequently gunned
RSC/GADSDEN BOF	Full combustion to evap. cooler and ESP									
No. 1 Vessel	No lance hole cover	254 (540,000)	7.1 (15,000)	1.8	94	18	405	90	6,900	Old lining gunned frequently on Vessel No. 1
No. 2 Vessel	W/lance hole covers				88	7.6	198	40	1,300	New lining burned in 2 days prior to study on Vessel No. 2
USSC/GARY NO. 1 BOF	Full combustion to quenchers and wet scrubbers									
Mary		307^d (650,000)	9.4 (20,000)	2.7	57	24	252	100	3,400	Multiple vessel operation. Isolation damper on Daisy partially closed (85% open)
Evelyn					45	20	216	60	1,900	
Daisy					63	28	286	90	5,000	
INLAND/IND. HARBOR NO. 4 BOF	Full combustion to wet scrubbers steam ring on									
Vessel 50	Lance holes on both vessels	228^e (484,000)	12.3 (26,000)	2.9	100	30	961	95	29,000	Both vessels had holes and large gaps in primary hood and exhaust ducting. The condition of ducting on Vessel 50 was worse than Vessel 60.
Vessel 60					100	19	890	40	17,000	
GLS/ECORSE (2 Vessels)	Full combustion to ESP. W/lance hole covers. Both vessels)	NA^f	9.4 (20,000)	NA	100	14.3	150	75	2,100	
FORD STEEL BOF (2 Vessels)	Full combustion to ESP	220^g (465,000)	11.3 (24,000)	2.0	69	8.0	162	60	890	

[a] Probable opacity duration product is equal to the product of the percent of oxygen blows showing emission times the average duration and opacity of emissions.

[b] Measured at scrubber stack (saturated) at 79°C (175°F) and atmospheric pressure.

[c] Measured at ESP stack (saturated) at 163°C (325°F) and atmospheric pressure.

[d] Installed fan capacity for all three vessels at scrubber outlet (saturated) -146 mmHg (-78 in. W.C.) at 110°F.

[e] Stack flow measurements at wet scrubber outlets (saturated at 53°C (128°F) and atmospheric pressure.

[f] Reliable estimates not available.

[g] Measured at outlet stack (dacfm) March 1979.

Process Observations and Oxygen Blow RMVEs. Even though the comparison of primary exhaust flow rates for all shops did not show strong correlations with oxygen blow RMVEs, it is generally accepted that higher exhaust rates should produce lower RMVEs in most situations. At USSC/Gary, the No. 1 BOF control system is shared by three vessels labled Daisy, Mary and Evelyn. During oxygen blow periods on Daisy, the isolation damper opened to only 85 percent of maximum. The lower exhaust flow on vessel Daisy corresponded to increased oxygen blow RMVEs compared to the other two vessels as shown in Table 6.

Spray Patching Impacts on Oxygen Blow RMVEs. RMVEs were observed to increase significantly when a vessel was spray patched prior to a heat. For example, RMVEs from the oxygen blow on one vessel at Gary that had just been extensively patched were two to three times higher in opacity and duration as compared to nonpatched heats. At Gadsden, the lining on No. 1 vessel was nearing the end of its campaign and was frequently patched. More oxygen was blown to account for the greater heat loss through the worn lining. However, lack of lance hole covers on this vessel caused heavy oxygen blow emissions, masking an increase that may have been attributable to patching.

TABLE 6. COMPARISON OF PRIMARY EXHAUST HOOD DRAFT WITH OXYGEN BLOW RMVEs AT USSC GARY No. 1 BOF

Vessel	Average hood draft[a] (in. H_2O)	Opacity - duration product[b] (% opacity-sec)
Daisy	6.2	5,045
Mary	8.2	3,450
Evelyn	8.3	1,904

[a] For all heats with available data; static pressure measured in quench section.

[b] Opacity - duration product is the product of the percent of oxygen blows showing emissions >0 times the average opacity and average duration of emissions from those oxygen blows.

Effect of Steel Chemistry. Oxygen blow RMVE may also be affected by the final steel chemistry. For example, high carbon steel heats at Gary showed RMVE for 80 percent of all oxygen blows, compared to the shop average of 50 percent of all heats. Conversely, low carbon heats produced the lowest RMVE. The oxygen flowrates were about the same for both high and low carbon heats, but the blow duration was less for the high carbon heats. One would almost expect higher emissions for heats where more carbon was oxidized (i.e., low carbon heats), but the exact opposite was observed at Gary.

Hot Metal to Scrap Ratios. Several BOF operating personnel have commented that high hot metal to scrap ratios generally cause more bath turbulence and fume escape during a blow. However, a review of process data for individual heats within each shop, and comparison of each shop to the others found no correlations.

Manual versus Automatic Control of Blow Rate and Lance Height. Manual control of lance height and oxygen blow rates was observed to significantly reduce bath turbulence and fume escape at Gadsden. All of the other shops relied on the normal operating procedure of automatic control, regardless of hood capture efficiencies. At Gadsden, increased turbulence during the critical period contributed substantially to oxygen blow RMVEs. On several occasions the melter reduced emissions during the critical period by decreasing the oxygen blow rate and raising the lance to retard the reaction rate in the vessel. When these emissions abatement practices were employed, GCA visible emissions observers verified substantial decreases in RMVEs by radio contact with in-shop observers. RSC/Gadsden indicated that oxygen blow rates at that shop can be reduced to approximately 12,000 scfm without causing excessive cooling of the bath.

Vessel Turndowns

After the oxygen blow, vessels are turned down for sampling of temperature and bath chemistry. Additives are sometimes placed in the slag layer of the bath to retard slag foaming and make sampling easier. Slag-conditioning addititives at various shops included: (1) blocks of green wood, (2) "Slag-Mag" cartridges, and (3) elemental sulphur. After sampling, vessels return to the vertical position for: (1) reblow if the bath temperature is low and/or the carbon is too high, (2) vessel rocking if the temperature is too high, or (3) idle mode awaiting return of the chemistry analysis. The TD duration was usually limited to 2 to 3 minutes at the six shops, although some TDs lasted over 15 minutes.

At the five top-blown BOF shops, TD emissions control was limited to use of the primary hood systems (often dampered to 20 to 30 percent open). Only the Q-BOP employed full exhaust rates and use of a secondary collection hood during TD. For all six shops, capture of TD emissions was less than 50 percent, and in most cases, zero capture was observed.

Turndown RMVE data in Table 7 indicates greatest TD emissions at USSC/Gary and Inland's No. 4 shop. The lowest turndown RMVEs were observed at RSC/Gadsden. At Gadsden, RMVE occurred for only 1 TD of 60 observed. Turndown RMVEs from the Q-BOP were moderate as compared to the other shops. Increased TD emissions capture at the Q-BOP was offset by increased emissions created by purge gases (nitrogen, oxygen and natural gas) blown through the tuyeres. RSC reports that nitrogen is normally used as a purge gas, but oxygen and natural gas were blown for 24 of 33 TDs observed. The data in Table 7 indicate that TD RMVEs were heavier when oxygen and natural gas were used.

TABLE 7. VESSEL TURNDOWN DATA AT SIX BOF SHOPS

BOF shop	Emissions control during turndown	Percent of turndowns showing RMVEs > 0 (%)	Average opacity of RMVEs > 0 (% opacity)	Average duration of RMVEs > 0 (seconds)	Peak RMVE (% opacity)	Opacity duration product[a] (% opacity-sec)	Comments
RSC/Chicago Q-BOP	Primary and secondary hoods operating	78	13	42	30	440	Nitrogen blown through tuyeres.
		83	17	43	65	620	Oxygen and natural gas blown through tuyeres.
RSC/Gadsden BOF	Primary hood only	1.7	5	30	10	2.5	Wood blocks added.
USSC/Gary No. 1 BOF	Primary hood only	73	18	98	75	1300	Slag-mag added.
Inland Steel No. 4 BOF	Primary hood only	67	18	142	65	1700	
GLS/Ecorse No. 2 BOF	Primary hood only	21	16	73	100	250	Elemental sulphur added.
Ford/Dearborn BOF	Primary hood only	33	10	83	20	270	

[a] Opacity duration product is the product of the percent of turndowns with RMVEs > 0 and the average opacity and duration of those RMVEs.

A review of process variations which might affect turndown RMVEs included the following; (1) vessel additions; (2) turndown duration; (3) slag conditioning additives. No correlations were evident between turndown RMVEs and vessel additions or TD duration.

A moderate correlation between slag conditioning additives and turndown RMVEs was observed from data collected at USSC/Gary. The slag conditioning additives used at the Gary No. 1 shop were a mixture of rock salt, sawdust and sulfur, called "Slag-Mag." In-shop observers counted the number of cartridges thrown into the vessel for several TDs. Figure 1 shows the duration of RMVE as a function of "Slag-Mag" cartridge additions, indicating that RMVE durations increased with increased "Slag-Mag" additions. It was not clear, however, whether the Slag-Mag reduces flames and foaming thereby creating heavier (smoke) emissions, or whether more cartridges are added to TDs with heavier emissions.

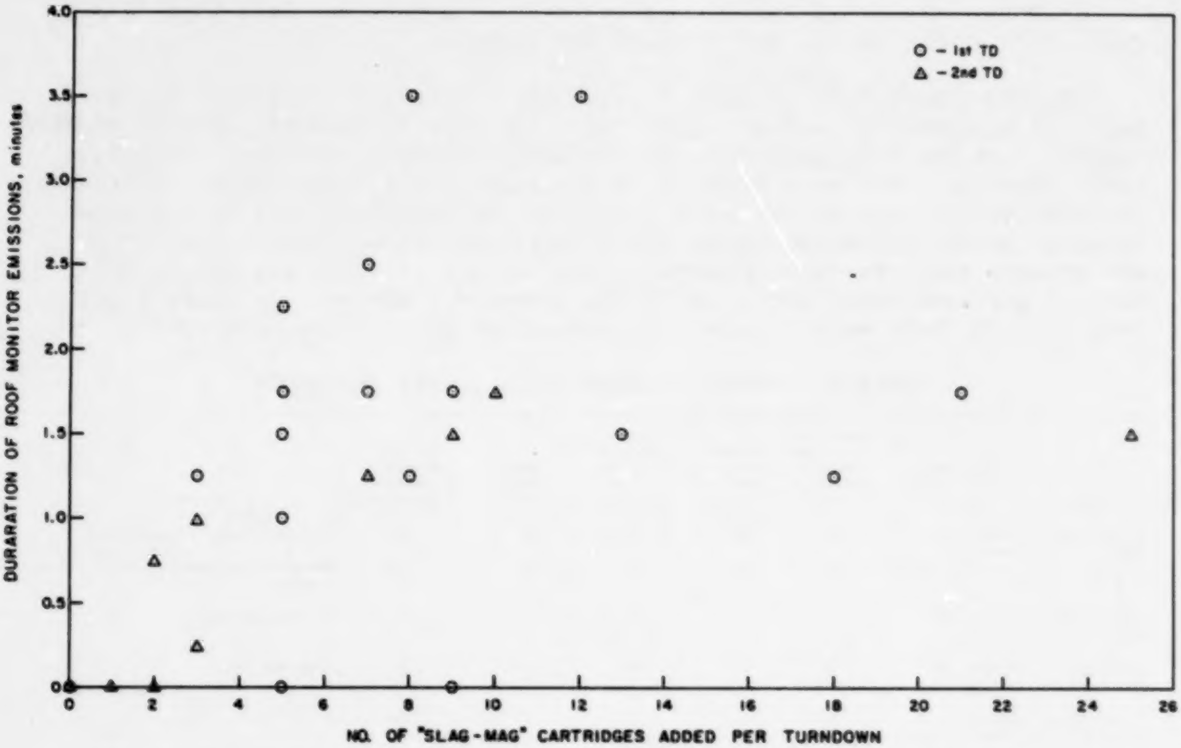

Figure 1. Relationship of "Slag-Mag" cartridge additions to RMVEs at USSC/Gary No. 1 BOF Shop.

Tapping

Once the desired steel temperature and chemistry are achieved, vessels are rotated to the tap position to deliver the heat. During tapping, alloys and other additives are metered into the ladle to achieve the desired steel chemistry. Taps generally lasted from 3 to 12 minutes. During tapping at the Q-BOP, nitrogen gas is blown through the tuyeres at 0.85 m^3/sec (1800 scfm) to prevent plugging.

Tapping emissions control at the six shops include two shops with no controls, three shops with tap-side enclosures, and the Q-BOP which employs the charge-side hood for tapping control. The data in Table 8 show the highest RMVE for shops with no tap-side enclosures, and the Q-BOP. Fume capture is reduced at Ford and Inland because control systems operate at reduced draft and the lack of tap-side enclosures or other containment devices. Capture of tapping emissions at the Q-BOP was somewhat reduced because the single secondary hood is located on the charging side. Tapping fumes escaped through a loose fitting door on the tap-side of the doghouse enclosure in spite of an exhaust rate of nearly 123 m^3/sec or 260,000 scfm. Recent designs of doghouse enclosures include tap-side hoods to improve tap control.

The data in Table 8 indicate that the three top-blown BOF shops with tap-side enclosures showed the lowest tapping RMVEs. RSC/Gadsden produced the lowest RMVEs, probably because of the relatively high exhaust rates (47.7 m^3/sec or 101,000 scfm). RMVE at USSC/Gary and GLS/Ecorse resulted from the escape of emissions out the charge side of the vessel. Increased exhaust rates may increase tapping control at these latter two shops. However, engineers at Gary indicated that introduction of cold air would adversely affect emissions capture at other online vessels.

TABLE 8. TAPPING DATA FOR SIX BOF SHOPS

BOF shop	Emissions control during tapping	Estimated emissions capture (%)	Tap ladle additions Kg (lb)	Percent of taps showing RMVEs > 0 (%)	Average opacity of RMVEs > 0 (% opacity)	Average duration of RMVEs > 0 (seconds)	Peak RMVE (% opacity)	Opacity[a] duration product (% opacity-seconds)	Comments
RSC/CHICAGO Q-BOP	Secondary hood only	0-50	3350 (7400)	75	9.8	368	85	2700	Desulfex ladle additive N_2 gas blown through tuyeres
RSC/GADSDEN	Primary hood w/ tapside enclosure	65	2430 (5400)	10	5.9	116	20	68	Exhaust rate 60-70% of max.
USSC/GARY NO. 1 BOF	Primary hood w/ tapside enclosure	0-80	620 (1350)	74	14	175	60	1800	Isolation damper 20% open
INLAND STEEL NO. 4 BOF	Primary hood only	0-20	NA[b]	100	18	223	50	3600	Minimal or zero exhaust
GLS/ECORSE NO. 2 BOF	Primary hood w/ garage door tap-side enclosure	30-70	NA	58	14	174	60	1400	-
FORD/DEARBORN BOF	Primary hood only	<50	1600 (3530)	83	11	275	70	2500	Isolation damper 30% open

[a] Opacity duration product is the product of the percent of turndowns with RMVEs > 0 and the average opacity and duration of those RMVEs.

[b] Not available.

Factors that may affect tapping emissions were assessed at three of the shops. Tapping emissions at RSC/Gadsden and USSC/Gary showed no strong correlations between RMVEs and the following process parameters: (1) total tap duration; (2) tap ladle additions; (3) steel temperature; (4) quantity of steel tapped.

For the Q-BOP, the analysis showed a strong correlation between tapping RMVEs and the addition of a desulfurizing compound to the tap ladle. Tapping RMVEs reached 85 percent opacity and averaged 20 percent opacity, for heats receiving this compound. By comparison, tapping RMVEs averaged less than 5 percent opacity for heats not receiving this ladle additive.

Slagging

After tapping, furnaces are rotated back to the charge side to dump slag into pots located below the charging floor. Slagging generally lasted about 1 minute. Occasionally, the vessel was rocked back and forth to coat the vessel lining if linings were thin.

Control of slagging emissions is difficult because the vessel mouth is directed away from the primary hood. At the top-blown BOFs, almost zero capture of slagging emissions was observed. Emissions capture was more substantial at the Q-BOP because the vessel remains inside the doghouse. Table 9 summarizes the slagging RMVE data, showing the lowest emissions (0 opacity) were observed for the Q-BOP.

The following were assessed for possible relationships to slag RMVE: (1) slag duration; (2) steel tap temperature; and (3) quantity and type of flux additions. No significant correlations between slagging RMVEs and these process parameters were observed.

TABLE 9. SLAGGING DATA FOR SIX BOF SHOPS

BOF shop	Secondary emissions control during slagging	Percent of slags showing RMVE > 0 (%)	Average opacity of RMVEs > 0 (% opacity)	Average duration of RMVEs > 0 (seconds)	Peak RMVE (% opacity)	Opacity duration product[a] (% opacity-sec)
RSC/Chicago Q-BOP	Primary and secondary hood	0	0	0	0	0
RSC/Gadsden BOF	None	10	5.9	55	15	34.2
USSC/Gary No. 1 BOF	None	33	16	85	50	449
Inland Steel No. 4 BOF	None	100	14	56	45	784
GLS/Ecorse No. 2 BOF	None	13	20	113	50	294
Ford/Dearborn BOF	None	5	5	30	5	7.5

[a] Opacity duration product is the product of the percent of slags with RMVEs > 0 and the average opacity and duration of those RMVEs.

STATUS OF CASTHOUSE CONTROL TECHNOLOGY IN THE UNITED STATES, CANADA, AND WEST GERMANY IN 1980

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ABSTRACT

This paper provides an up to date review of recent developments in blast furnace casthouse control technology in the U.S. Six casthouse control systems were installed in the U.S. on a permanent basis by the fall of 1980. Three additional continuous-service casthouse control systems are operating in Canada. A number of prototype systems are under development and demonstration in the U.S. At this time the U.S. steel industry has made committments to install controls on at least 41 casthouses. The paper discusses current trends in the U.S. and also describes operating control systems in this country, Canada, and West Germany.

STATUS OF CASTHOUSE CONTROL TECHNOLOGY IN THE UNITED STATES, CANADA, AND WEST GERMANY IN 1980

INTRODUCTION

Casthouse emission control systems are installed on a permanent basis at nine North American blast furnaces as of the fall of 1980. Demonstration tests at four other casthouses are being conducted in order to obtain EPA approval of proposed systems. By the fall of 1980, the steel industry has made committments to EPA to retrofit controls to at least 41 furnaces, and discussions are presently being concluded on controls for another 17 furnaces. This paper provides the current status of casthouse controls in the U.S. and also discusses controls in Canada and West Germany. Descriptions of Japanese casthouse controls have appeared elsewhere in the literature.[1]

The principal problem with casthouse control technology, as stated by the industry, is the retrofit of existing furnaces. At this time, seven conventional furnaces in North America have retrofit control systems--DOFASCO's Nos. 1, 2 and 3, and four Bethlehem Steel furnaces. DOFASCO uses total building evacuation (TE) for three of their furnaces, but is planning to convert Nos. 2 and 3 to a local hood (LH) system. The Bethlehem B, C, D and E furnace have large canopy-type hoods in the roof trusses above the taphole and runners. All existing systems in North America use baghouses for gas cleaning.

Industry's main concern with retrofitting TE technology center around the costs of moving large air volumes, the difficulty in completely sealing a casthouse to prevent fume escape, and the need to structurally reinforce the roof. The LH option relies on relatively manageable air volumes, but the difficulty of fitting local hoods and routing ductwork within the confines of an existing casthouse varies from casthouse to casthouse. A secondary concern with the LH option is achieving efficient capture of casting emissions from the numerous potential sources, i.e., notch and troughs, runners, ladles, slag spouts, and slag pits or pots.

A number of experimental LH systems have been tried in the past at U.S. casthouses. This fall, several prototype systems are being demonstrated at the Edgar Thomson Works of U.S. Steel (LH), Wheeling-Pittsburgh Steel, Monessen Works (LH) and at three J&L Steel plants--Aliquippa, Indiana Harbor Works and Cleveland (noncapture shrouding technique). These systems are all retrofit to existing furnaces. The J&L technology is of interest nationwide, because it does not use exhaust fans or gas cleaning devices.

The two newest blast furnaces in the U.S. were designed with emissions control as one objective. Bethlehem's L furnace at Sparrows Point and the No. 7 at Inland represent the state-of-the-art of both iron-making and emissions control. Both furnaces have evacuated, covered runners, local hoods over the trough and iron spouts, and a baghouse. These new furnace controls are similar in concept to the casthouse controls developed in Japan and also used in West Germany. Certain design aspects of these large furnaces -

multiple tapholes, tilting iron runners, and ductwork running underneath the casthouse floor--are instrumental in achieving good control performance. These features are not present on most furnaces in the U.S. and could be added only during a major rebuild.

TOTAL CASTHOUSE EVACUATION (TE)

The first continuous-service TE control system on a basic iron-producing furnace in North America was retrofit to the DOFASCO No. 1 casthouse in 1975. A similar system entered service on DOFASCO's Nos. 2 and 3 casthouses in 1978. A ferromanganese-producing blast furnace operated by Bethlehem Steel in Johnstown, PA was fitted with a 400,000 acfm TE system in the mid-seventies. However, this furnace has been out of service since 1977.

U.S. Steel was committed to six TE systems in the Monongahela Valley (PA). However, the company has recently proposed local hoods instead, for these six blast furnaces. At DOFASCO, the Nos. 2 and 3 TE systems are being converted to the LH option. However, the conversion from TE is primarily to better utilize the existing 400,000 acfm baghouse which is shared by the two furnaces. At Bethlehem's Bethlehem, PA plant, partial evacuation systems were installed on four furnaces in the summer of 1980.

Although the current trend seems to favor the LH option, the TE concept may still be a favored alternative for smaller casthouses, as evidenced by DOFASCO's TE system on No. 1 furnace and the four Bethlehem partial evacuation systems. DOFASCO reports they are satisfied with their 5 years experience with the No. 1 TE system, and several U.S. companies are considering options for TE or partial evacuation at this time.

Existing TE Systems: DOFASCO Nos. 1, 2, and 3

The only online North American casthouses employing total evacuation are DOFASCO's Nos. 1, 2, and 3 furnaces. Table 1 provides a quick summary of casthouse size and evacuation rates.

TABLE 1. CHARACTERISTICS OF THE DOFASCO CASTHOUSES AND CONTROL SYSTEMS[2]

Furnace number	Rated capacity, nthm per day	Casthouse floor dimensions (ft)	Total enclosed volume (ft^3)	Design evacuation rate (acfm)	Air changes per minute
1	2,140	62 x 65	150,000	300,000	2.00
2	2,015	91 x 100	350,000	400,000	1.14
3	2,150	91 x 67	365,000	400,000	1.10

DOFASCO began experimenting with the No. 1 casthouse in 1975 with a TE exhaust rate of 250,000 acfm. A progression of improvements to increase performance were summarized as follows:[2]

- Improved sealing between the furnace and the bustle pipe to make the curtain wall separating the casthouse from the furnace shell fully effective.

- Sliding cover at the scrap hole opening over the railroad tracks to prevent short circuiting by air entry at this point.

- Sliding doors over the slag pit openings.

- Counterweighted panels along the western (prevailing wind) casthouse wall to allow closure of sidewall openings during casting.

- Considerable flashing to seal the building and prevent fume leakage.

- Increasing the fan exhaust flow rate to 300,000 acfm (flow rate was measured at 340,000 acfm, maximum in 1976[1]).

Before the above steps were implemented, DOFASCO reported that the baghouse catch averaged 0.3 lb/ton of iron cast. After the casthouse was "tightened up," DOFASCO measured 0.6 lb/ton (5-month average).[2] Method 5 testing conducted for EPA in 1976 measured 0.6 lb/ton at the baghouse inlet on No. 1 furnace.[1]

Maximum temperature on the cast floor during casting ranges from 37° to 48°C, a level acceptable to DOFASCO.[3] A study of personnel exposure to respirable suspended particulate (5 microns), total suspended particulate, sulfur dioxide, and carbon monoxide found that the casthouse control system on furnaces Nos. 1, 2, and 3 did not change exposure levels, compared to the uncontrolled casthouses.[2]

The No. 1 baghouse is a single compartment, positive pressure unit with a design air-to-cloth ratio of 2.5:1 at 250,000 acfm. It has 2,160 polyester bags measuring 8 inches in diameter and 22.5 feet in length. A bypass stack between the fan and the baghouse protects bags in case of excessive inlet temperatues, and also provides the exhaust during bag cleaning.

After the No. 1 TE system was completed, a similar TE system was installed at the Nos. 2 and 3 blast furnaces in 1978. DOFASCO anticipated that casting could be sequenced so only one furnace was casting at any one time. Thus, one baghouse and fan serves both furnaces as shown in Figure 1. The Nos. 2 and 3 control systems are similar to the No. 1 furnace, with minor differences noted below.

At the No. 3 casthouse, the curtain wall, roof plenum and roof reinforcement were installed during a furnace reline period, in a fashion similar to the No. 1 casthouse. However, construction of the No. 2 system was simplified over Nos. 1 and 3, and completed while No. 2 furnace was in service. The No. 2 system has a lighter roof load and lighter weight curtain wall. This weight

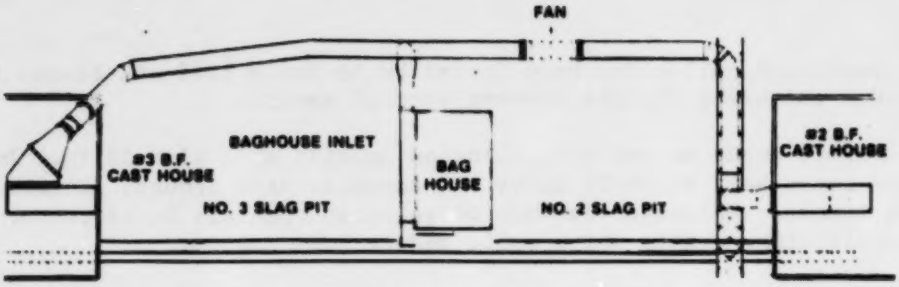


Figure 1. Plan view of No. 2 and No. 3 casthouse fume control system.[2]

reduction, and corresponding cost reduction, was accomplished by the following design changes:[2]

- Supporting the 10-foot diameter exhaust duct from a structural steel bridge spanning the slag pit, as opposed to laying the duct on the casthouse roof as was done on Nos. 1 and 3. This reduced the extent of additional roof reinforcement.

- The roof plenum intake duct on No. 2 was kept as small as possible and fabricated from 1/4-inch plate to eliminate additional structural support steel on the casthouse roof.

- The curtain wall on No. 2 was constructed of prefabricated framing panels that were presteeled with corrugated stainless steel prior to installation. Curtain walls on Nos. 1 and 3 were framed in placed and covered with 1/4-inch plate.

The above weight reduction steps also reduced No. 2 furnace shutdown requirements to 21 8-hour days, compared to 46 8-hour shutdowns which would have been required to construct a TE system identical to Nos. 1 and 3.

The single compartment, positive pressure baghouse serving Nos. 2 and 3 casthouses has an air-to-cloth ratio of 3.3:1 at 400,000 acfm. The 1,360 polyester bags each measure 11-3/4 inches in diameter and 30 feet 7 inches in length. The exhaust fan is designed for 400,000 acfm at a static pressure of 16 in. W.G., using a 2,500 hp, 900 rpm direct drive motor. When not casting, the fan idles with dampers partially closed.

The Nos. 2 and 3 casthouse control system entered service in November 1978. DOFASCO's data for 28 February 1979 to 18 March 1979 shows the average baghouse catch was 0.702 lb per ton of hot metal.[2]

Existing Partial Evacuation Systems: Bethlehem's B, C, D, and E Furnaces

A partial evacuation (PE) control system was installed in the summer of 1980 at blast furnaces B, C, D, and E at Bethlehem Steel's Bethlehem PA plant. Each PE system consists of a single canopy hood located in the roof trusses above the iron notch, trough, and runner areas. The system design is based on experiments conducted in 1977 on Bethlehem's E furnace. The first generation collection hood installed on the E furnace in 1976 proved unworkable.[4]

A second generation collection hood installed in early 1977 and tested in late 1977 provided the basis for the current control system.

The capture hoods at the four furnaces consist of a 21 × 56-foot hood in the roof-truss bay, directly above the taphole, main trough, skimmer, and upper slag runner. Permanent closure of selected openings in casthouse side walls controls cross drafts which could reduce hood capture.

A single baghouse provides gas cleaning for all four furnaces. When one furnace is casting, a single fan provides the design evacuation rate of 390,000 acfm. The other three furnaces are dampered off. When two furnaces are casting, two fans provide a design evacuation rate of 330,000 acfm per furnace. A backup fan of 200,000 acfm was also installed. Normal hot metal production is as follows: B - 2,900 tpd, C - 2,700 tpd, D - 3,200 tpd, and E - 2,150 tpd.

LOCAL HOODS RETROFIT TO CONVENTIONAL FURNACES

Interest in local hoods (LH) has stemmed from the premise that exhaust flowrates (and, thus, capital and operating costs) would be considerably less than for the TE option. This is especially important for larger casthouses that may require above half a million acfm to provide the number of casthouse air changes thought to be necessary for adequate control (i.e., 1.1 to 2.0 air changes per minute as at DOFASCO). The primary industry concerns with retrofit LH systems are ductwork routing within the available space, interference with casthouse operations (drilling, mudgun, working of runners, runner maintenance), decreased capture efficiency because of cross drafts, and possible lack of space for adequately-sized hoods and/or ductwork.

At present, no retrofit LH systems are operating in the U.S. on a continuous basis. However, Wheeling-Pittsburgh Steel's Monessen plant has a planned start-up date of November 1980 with local hoods on one furnace. In addition, several steel companies are committed to retrofitting LH on a number of casthouses.

Planned LH Systems: Wheeling-Pittsburgh, Monessen, PA

Wheeling-Pittsburgh Steel will be demonstrating a LH system at the Monessen plant. The proposal calls for local hoods over the iron trough area and four local hoods above each of the four iron spouts. The hoods will be evacuated to a 130,000 acfm baghouse. A demonstration-type system is scheduled to start up in November 1980 on the No. 3 blast furnace and will be evaluated by EPA at that time.[5] If approved, this system will be retrofit to all three Wheeling-Pittsburgh facilities.

Proposed LH Systems: U.S. Steel

U.S. Steel is proposing to retrofit LH controls with noncapture techniques on a number of their casthouses. The control plan is to retrofit LH to seven plants in the Monongahela Valley and to three furnaces at the Geneva, UT plant. Discussions with EPA for LH controls at other U.S. Steel plants are currently underway.

In the Monongahela Valley complex, U.S. Steel has proposed to use LH instead of TE for seven casthouses. The company is currently experimenting with a local hood at the Edgar - Thomson No. 1 blast furnace. The proposed system consists of a notch-area hood under the bustle pipe, extending over most of the iron trough. A blower system is planned to help direct trough-area emissions into the hood. Noncapture techniques are being proposed for controlling the rest of the casthouse. Total exhaust flowrate for the trough area hood is presently 140,000 acfm, with one baghouse per furnace. EPA is presently evaluating the proposed hood at the Edgar Thomson plant.

Other Proposed or Planned LH Systems

National Steel is proposing to use local hoods above the iron spouts and a trough area enclosure for controlling casthouses at the Weirton, Granite City and Great Lakes plants. Additional information is not available at this time.[6]

American Air Filter recently announced receipt of a turnkey order from U.S. Steel to install a LH control system on the No. 8 blast furnace at Fairfield, Alabama. Local hoods and runner covers will be installed on this two-taphole furnace. Total evacuation rate is reportedly 300,000 acfm. An off-line cleaned baghouse designed for an outlet grain loading of 0.010 gr/ft^3 will be used.[7]

DOFASCO's Conversion of Nos. 2 and 3 to LH from TE

DOFASCO is studying the conversion of the Nos. 2 and 3 TE systems to an LH system to avoid the occasional operation of an uncontrolled furnace. As mentioned previously, Nos. 2 and 3 furnaces share a baghouse. The original plan was to stagger casting schedules so only one furnace was cast at any one time. Casts overlap to some extent, and whichever furnace is cast second operates uncontrolled.

DOFASCO is planning to use LH over the taphole and torpedo cars with a net evacuation rate of 200,000 acfm per furnace. This would allow the 400,000 acfm baghouse, originally designed to handle one furnace with TE control, to handle both furnaces simultaneously. Hooding is currently being installed on the No. 2 furnace which is down for reline (Fall 1980). Both furnaces will be converted to two-taphole runner systems.[3]

Stelco's Experience with LH

Stelco operates four blast furnaces at the Hilton Works in Hamilton, Ontario. A prototype system was recently installed on one furnace, consisting of an iron trough hood and baghouse. Stelco is committed to installing controls on the remaining three furnaces, although there is no installation schedule at present.

Stelco's Lake Erie plant has one new, 5500 tpd blast furnace with local hoods over the iron trough and iron spouts, with runner covers. Apparently, the casthouse is considered in compliance with applicable regulations, although formal compliance tests have not yet been conducted.[8]

LOCAL HOODS ON NEW FURNACES AND LARGE RETROFIT FURNACES

Although this paper primarily discusses casthouse control technology in the U.S., Canada, and West Germany, brief mention will be made of other country's experiences. Virtually 100 percent of all Japanese blast furnaces have casthouse controls, of which some are retrofit and some are new furnaces.[1,9] Four large furnaces in the Rhine-Ruhr region of Germany were retrofit with LH and evacuated runner cover controls in the late seventies. Two other furnaces also have control systems. The same type of technology was employed at the two newest blast furnaces in the U.S.--the L furnace at Sparrows Point, and the No. 7 furnace at Inland. DOFASCO is installing similar systems on their 4,000 tpd No. 4 furnace. The newer Japanese systems differ somewhat from the West Germany and new U.S. furnaces in that the new Japanese systems control drilling and plugging emissions by a scavenger hood with curtains that lower around the taphole area.

Casthouse controls are also being developed in France, Italy, England and Sweden; at least one controlled casthouse operates in each country. Italsider in Taranto, Italy operates a system consisting of side draft hoods on the iron notch area, runner covers, and iron spout hoods. The British Steel Corporation operates a control system at the Middleboro plant consisting of runner covers and iron spout hoods, complemented with curtains. In France, the Usinor-Dunkerque plant is also installing casthouse controls.[6]

The new and retrofit LH systems on the large blast furnaces in the U.S., West Germany, Canada, and Japan operate in relatively large casthouses which generally have adequate internal space for hoods and ductwork. These casthouses have several features not generally present on older U.S. furnaces; i.e., multiple tapholes, tilting iron and slag runners, and casthouse floors suspended on columns which allow for ductwork routing underneath the floor. Applicability of these LH systems to older U.S. casthouses may be limited without extensive rebuild. Applicability must be judged on an individual basis.

New Furnace Control in the U.S. - Sparrows Point and Inland

The two newest blast furnaces in the U.S. recently entered service with casthouse controls consisting of local hoods and evacuated runner covers. Bethlehem's L furnace at Sparrows Point and Inland's No. 7 furnace differ from older furnaces in the U.S. in production capacity, charging and casting methods, and top pressure. Where older furnaces are rated at about 1000 to 2000 tons/day of hot metal, the new furnaces produce about 10,000 tons/day. Most older furnaces have one taphole located in a single casthouse, while the new approach is four tapholes located within two casthouses.

The new furnaces are cast almost continuously, rotating hour-long casts between tapholes. The fourth runner system is usually off-line for relining or maintenance. The new furnaces operate under a top pressure of several atmospheres. Iron is cast into multiple ladles through tilting iron runners. Burden is charged continuously through a bell-less top via a belt conveyor.

The new furnace's emission control systems are similar in concept to the West German plants, described below. Troughs and runners are covered, and interconnected to exhaust hoods located at key points: taphole, skimmer/dam, and tilting iron runners. The exhaust ducts pass from hoods directly downwards through the casthouse floor, and join common ducts leading to the baghouses. The casthouse floors rest on columns, and torpedo cars travel underneath. This contrasts to some older furnaces where the casthouse is backfilled; i.e., there is no open space underneath the floor.

The iron runners are fairly deep at the new furnaces. This allows for flat runner covers, with an arched section used on the trough and/or spouts. The arched section is removed for drilling and plugging. The total exhaust flowrates are reportedly 300,000 acfm at Sparrow's Point, and at Inland's No. 7 furnace, 320,000 acfm.

Retrofit LH Systems in West Germany

All of the six controlled casthouses operating in the Rhine-Ruhr region of West Germany use the LH option. Only the larger furnaces (5,000 to 10,000 tonnes/day) are controlled. The six controlled furnaces represent 25 percent of West Germany's iron production.

GCA observed four of the six controlled casthouses. The two controlled furnaces not observed are operated by Thyssen; one produces ferromanganese, while the other has a control system not yet completed. Table 2 provides an overview comparison of the four casthouses of interest. It is important to note that all four furnaces observed in West Germany are the pressure-type; i.e., the top pressures are 2+ atmospheres. Highlights of the plant visits appear below.[10]

Krupp-Rheinhausen No. 1 Furnace. This retrofit casthouse has side draft hoods on the taphole and the torpedo car. A hinged taphole hood extension lowered over the iron pool is raised for drilling and plugging. The slag runner, slag pots, skimmer/dam area, and the iron runner are uncontrolled. This furnace has two tapholes and two casthouses.

According to regulatory officials, about 80 percent total capture is normally obtained with this system. Regulatory officials feel this is the least effective design in the region because of the following factors:

- Low exhaust flowrate.
- No control of skimmer and end of iron pool.
- Uncovered iron and slag runners.
- No slag pot control.
- Casthouse sides are open and cross drafts tend to reduce capture efficiency.

TABLE 2. SUMMARY OF WEST GERMAN CASTHOUSE CONTROL SYSTEMS

Firm	Plant	Daily production, metric tpd	Year furnace entered service	Year control system entered service	No. of tapholes	No. of cast-houses	Capture system	Gas cleaning system	Total exhaust applied to hood system m^3/hr[b]	Estimated capture efficiency[d]
Krupp	Rheinhausen	5,000	1976	1977	2	2	Side-draft hood, both sides of taphole. Side-draft hood, both sides of torpedo car. No control for slag runner, iron runner or skimmer. No runner covers.	Scrubber[c]	320,000	80
Thyssen	Hamborn No. 4	5,000	1964[a] (1975)	1978	2	2	Three hoods, over taphole, dam and skimmer, and tilting iron runner. No slag runner or slag pot control. No runner covers.	Baghouse	580,000	80
Thyssen	Schwelgern No. 1	10,000	1973	1975	4	2	Hoods above taphole and iron pool. Hood over dam, skimmer, tilting iron runner. Iron runner covers. No control of slag runner.	Baghouse	700,000	95
Mannesmann	No. A	6,000	1973	1978	2	2	Runner covers over iron and slag runners and iron pool. Covers connected to three hoods, at dam/skimmer, tilting iron runner, and tilting slag pot runner. Scavenger offtakes in roof canopy above cast floor.	ESP	716,000	99+

[a] Conflicting data.

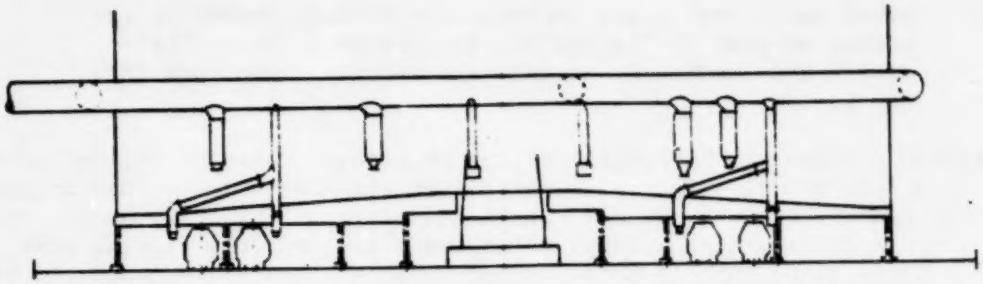
[b] "Normal," standard m^3/hr.

[c] Scrubber reportedly selected over baghouse or ESP due to space restrictions and availability of excess sludge handling capacity.

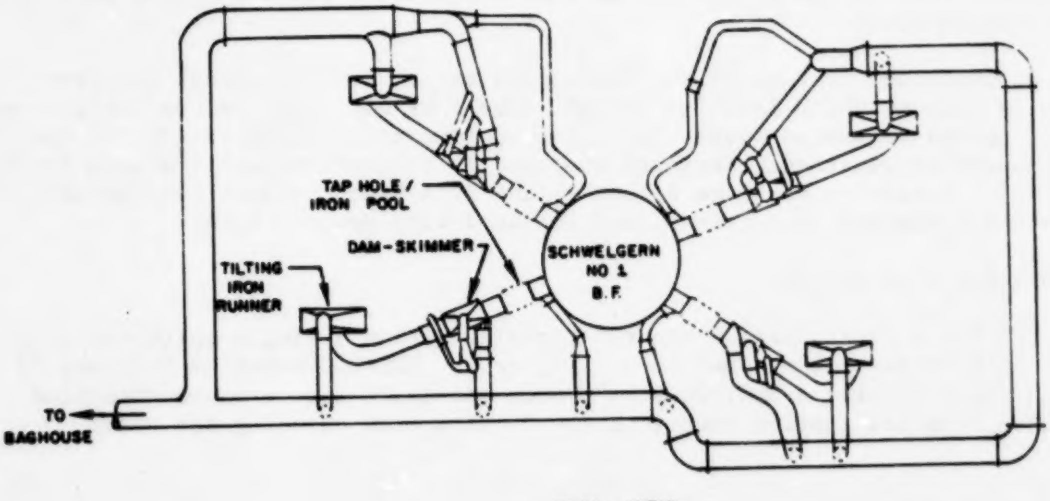
[d] Estimates based regulatory officials' assessment of normal operation, supplemented by GCA's observations.

Thyssen - No. 4 Hamborn Furnace. This furnace has two relatively small casthouses, and both the regulatory authorities and Thyssen feel the system is the best achievable due to retrofit problems. Thyssen would prefer to increase the taphole flowrate, but space restrictions limit the ductwork diameter. Observation of one cast found the following. The tilting iron runner and the skimmer/dam hood both showed 95+ percent capture. The slag runner, slag pot and iron runner were uncontrolled, but showed only light emissions of 10 to 20 percent opacity as observed inside the casthouse. Most of the emissions escaped from the taphole area. Regulatory officials feel that this system normally provides capture of about 80 percent of total casting emissions.

Thyssen-Schwelgern No. 1 Furnace. Considered the second-best control system in the region, this furnace is controlled by local hoods above the tapholes, the dams and skimmers, and the tilting iron runners. Refractory-lined covers completely enclose the iron runners and connect with the three hoods. The slag runner is uncontrolled. The system layout appears in Figure 2.



CROSS-SECTION



PLAN VIEW

Figure 2. Emission control system of Thyssen-Schwelgern No. 1 casthouse.

Regulatory officials reported that capture efficiency is normally 95+ percent, but there are usually some small leaks in the hood system. Thyssen would like to increase the total exhaust from 700,000 N m^3/hr to about 1.0×10^6 to improve taphole control, and use Mannesmann-type SiC runners to decrease runner maintenance. The runner material currently used at Schwelgern requires relining once per week. Other than these modifications, both Thyssen and the regulatory authorities are satisfied with the system.

Mannesmann A Furnace. This retrofit system is the best-performing casthouse control system in West Germany according to regulatory officials. Observation of one complete cast, tap to plug, found almost no visible emissions escaping the runners or taphole, as viewed inside the casthouse. The only emissions that escaped the control system were as follows:

- One to two minutes of emissions when the iron trough cover was removed for a drill, redrill or plug.
- Minor puffs that occur infrequently through joints in the runner covers. Puffs rapidly dissipated to 0 opacity within the casthouse, or were immediately drawn back into the system.

Figure 3 shows the Mannesmann system of arched, refractory-lined covers on all portions of the iron pool, iron runner and slag runner. Casting emissions are contained by the runner covers and drawn off by three hoods, one each over the tilting iron runner, the skimmer area and the tilting slag runner. There is no taphole hood, and no visible emissions escaped the taphole area during normal operation. Should any emission escape the system, the exhaust flow can be manually diverted to three or four scavenger ducts located in an overhead canopy formed by steel sheeting on the roof trusses. Mannesmann reported they will use an almost identical control system when the B furnace is built.

An important feature of the Mannesmann system is the precast SiC iron and slag runners which last for 200,000 tonnes of hot metal before replacement. Runner covers are moved weekly for runner maintenance. Slag buildup on the SiC runners is reportedly lessened compared to conventional silica sand lining material. Excessive downtime during reline is avoided because the precast runners are removed in sections, and replaced with new sections.

DOFASCO No. 4 LH System

The No. 4 blast furnace has two tapholes within a single casthouse that has a much larger volume than Nos. 1, 2, or 3. DOFASCO reported that the TE option would require a 600,000 acfm system and would likely cause crossflow of fumes from the casting runner to the furnace crew cleaning the other runner.[2]

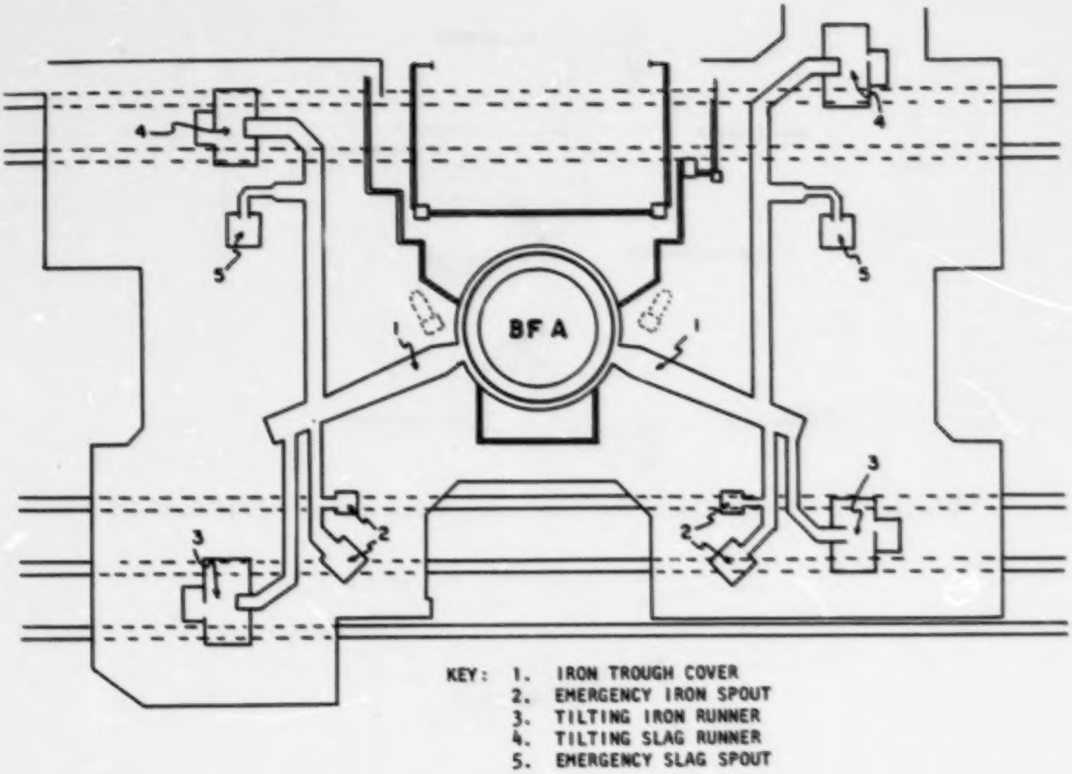


Figure 3. Plan view of the controlled casthouses at the Mannesmann "A" furnace.

DOFASCO selected a system of localized hoods over the two tapholes and the two tilting runners as shown in Figures 4, 5 and 6. These four hoods will be connected to a common duct leading to a fan and a baghouse when the system is completed in 1981. The original concept called for an air curtain to push iron trough emissions into the taphole hood. DOFASCO's current plan (Fall 1980) is to use covers for iron runner control.

The tilting runner design allows for a shorter iron runner length compared to a fixed runner design. DOFASCO reports that without the tilting runner, total iron runner length would be 75 feet per taphole compared to 24 feet per taphole with the use of the tilting runners. The shorter runners theoretically reduce fume generation by reducing hot metal exposure to air. Runner maintenance is also reduced. A captive locomotive was necessary to place the additional torpedo car under one side of the tilting runner. The locomotive normally used for casting positions ladles on the other side of the runner.

DOFASCO reports several advantages with the LH approach in a large casthouse, compared to TE; i.e.:[2]

- Fumes are collected at the source and better working conditions are achieved.

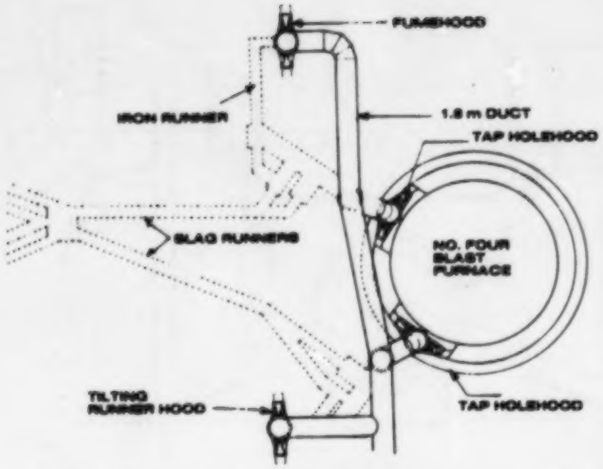


Figure 4. No. 4 blast furnace casthouse fume collection.[2]

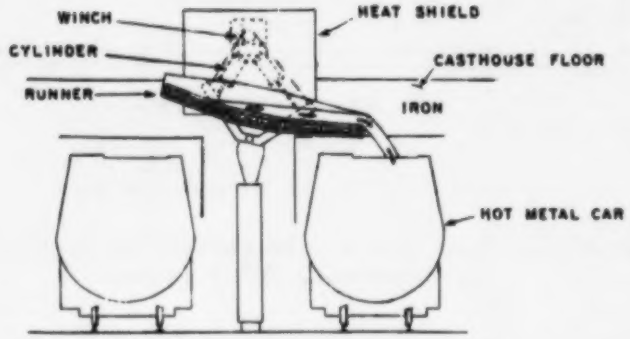


Figure 5. Tilting runner-No. 4 blast furnace.[2]

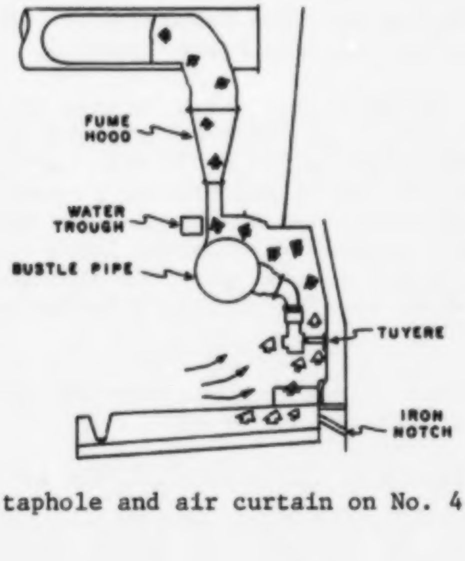


Figure 6. Local taphole and air curtain on No. 4 blast furnace.[2]

- The fume collection system is smaller, with respect to gas volume and capital construction costs.

- There is minimal interference with furnace operation.

DOFASCO indicated that efforts to reduce generation of iron pool emissions have included the consideration of reducing the taphole angle from 18 degrees to 12 or 15 degrees (measured from the horizontal) and to reduce the drill bit size to 1-7/8 inches. Both of these modifications would tend to reduce iron pool turbulence and theoretically reduce uncontrolled emissions.

NONCAPTURE TECHNOLOGY DEMONSTRATED BY J&L STEEL

J&L Steel is presently demonstrating a proprietary technology involving suppression of casting emissions by noncapture shrouding techniques. EPA contractors are presently evaluating emissions control performance of this technology at three J&L plants--Aliquippa, Indiana Harbor Works, and at Cleveland (Fall of 1980). All three systems were retrofit. The technology has generated interest because it does not rely on evacuation fans or gas cleaning devices. No further discussion is provided because the system design and operation details are considered proprietary.

SUMMARY OF AVAILABLE EMISSIONS DATA

Visible emissions (VE) data are available to describe the control performance of DOFASCO's three TE systems, and J&L's prototype systems. Limited VE data are available for the Bethlehem E furnace during demonstration tests. More VE data will become available as additional retrofit control systems come online in 1981-82. Mass emissions data describing the uncontrolled emission rates are available from DOFASCO, the Bethlehem E furnace and four West German casthouses.

Visible Emissions Data

Table 3 summarizes VE data for DOFASCO, Bethlehem E, and the three J&L casthouses. A more detailed emissions breakdown will be provided in the field test report for each plant.[11,12,13]

The 31 casts at DOFASCO were observed by test teams consisting of three environmental engineers, all certified to record VE by EPA Reference Method 9 (40 CFR 60.275 Part A). One engineer stationed inside the casthouse documented the origin and magnitude of all emissions generated during the entire cast. A second engineer recorded VE escaping the casthouse in accordance with Method 9. The third test team member continuously walked around the casthouse, searching for VE that may not be visible to the main VE observer. Constant FM radio contact enabled the test teams to document whether the Method 9 observer was viewing the greatest emissions.

For all casts observed at DOFASCO's Nos. 1, 2 and 3 furnaces, the hot metal sulfur averaged 0.054 percent by weight, ranging from 0.030 to 0.088. More detailed process data and emissions assessment appear in the Final Report.[11]

TABLE 3. SUMMARY OF VISIBLE EMISSIONS DATA FOR CONTROLLED CASTHOUSES

Casthouse	Test date	No. of casts observed	Percent of total Method 9 observations[b] 0-15% opacity	20-60% opacity	>60% opacity
DOFASCO No. 1[a]	5/80	10	93	7	0
DOFASCO No. 2[a]	5/80	9	95	5	0
DOFASCO No. 3[a]	5/80	12	74	26	0
Bethlehem E	10/77[c]	2	90	10	0
	10/77[d]	1	8	88	4
	10/76[e]	6	39	58	3
J&L-Indiana Harbor[f]	9/80	30	94	5	0.5
J&L-Cleveland[f]	10/80	50	95	5	0.03
J&L-Aliquippa[f]	11/80	21	97	3	0.1

[a] The DOFASCO data provided here excludes the last 5 minutes of each cast due to heavy plugging emissions that escaped capture. VE escaping the casthouses during plugging were ≥ 20 percent opacity for about 60 percent of all casts observed.

[b] Method 9 observations recorded at 15-second intervals.

[c] At ~300,000 acfm.

[d] At ~150,000 acfm.

[e] Experimental notch area hood, roof monitor emissions read by one observer.

[f] Results of preliminary data assessment. About 75 percent of emissions >60 percent opacity occurred during plugging and/or abnormal operations.

The J&L VE data were collected in a fashion similar to the DOFASCO data. The process data are considered confidential and are not available at this time.

Mass Emissions Data

Table 4 summarizes available mass emissions data for uncontrolled casthouse emissions that were captured by each control system. The DOFASCO data are based on several months of weighing the baghouse catch and is considered representative of their operation. The DOFASCO TE systems have been observed by GCA to capture on the order of 95+ percent of the total casting emissions. A testing program on the No. 3 casthouse is underway in November 1980 to obtain additional uncontrolled mass data and inhalable particulate data.

TABLE 4. MASS EMISSIONS DATA FOR UNCONTROLLED CASTHOUSE EMISSIONS CAPTURED BY CONTROL DEVICES

Plant	Date of measurement	Measurement technique	Uncontrolled emission rate, lb/ton of hot metal
DOFASCO No. 1	1977	Baghouse catch[a]	0.60
DOFASCO No. 1	1976	Method 5	0.60
DOFASCO Nos. 2 & 3	1979	Baghouse catch[b]	0.70
DOFASCO No. 3	1980	Method 5, IP	c
Bethlehem E[d]	1976	Method 5	0.24
Four West German Plants[e]	1978-79	VDI, mass balance	2.0

[a] Five-month measurement; Reference 2.

[b] Nineteen-day measurement; Reference 2.

[c] Method 5 and inhalable particulate tests conducted in November 1980; data not yet available.

[d] Hood capture unknown; see text.

[e] Data for large, pressurized furnaces, which likely generate more emissons than conventional furnaces; see text. VDI method is West Germany's standard mass emissions measurement technique.

The mass emissions data shown for Bethlehem's E furnace are the average of nine Method 5 tests on the duct serving the partial evacuation canopy hoods. The exhaust flowrates were varied from 175,000 acfm to 358,000 acfm during these tests. It cannot be determined what percent of total casthouse emissions were captured and sampled because the Bethlehem partial evacuation systems are not designed to capture emissions from all casthouse emission sources. VE data provided previously in Table 3 indicate some emissions escape this system and are emitted to the atmosphere.

The data from West Germany was obtained by direct sampling of inlets to control devices for three plants, and by measurement of scrubber solids for the fourth plant. The West Germans consider these data unrepresentative of a smaller, 2000 tpd plant for two reasons: (1) the data represent large (6,000 to 10,000 tpd) furnaces operating with a top pressure of several atmospheres, and these furnaces are considered to generate more notch area emissions than furnaces with about one atmosphere of top pressure; and (2) the high exhaust flowrate applied to the local hoods and covered runners is felt to increase the uncontrolled emission rate by increasing hot metal/air mixing.[10]

Not included in Table 4 are results of testing for uncontrolled casthouse emissions by using high volume samplers suspended in roof monitors. Because of several uncertainties associated with the accuracy of this test method, it is quite difficult to determine whether this technique can develop an accurate uncontrolled emission factor.

CONCLUDING COMMENTS

The diversity of concepts being evaluated by DOFASCO, J&L, U.S. Steel, National Steel, Bethlehem Steel and Wheeling-Pittsburgh Steel indicate there are many options for solving blast furnace casthouse problems, and that emissions controls may not be limited to only a few options. Furthermore, discussions with workers and operating personnel at DOFASCO, U.S. Steel and J&L indicate that a problem of worker and operator acceptance of control apparatus may not exist.

Future trends in iron-making are likely to change emissions characteristics of blast furnaces in the U.S. Large new furnaces, along with changes in smaller, existing furnaces such as use of external desulfurization, modest increases in hearth diameter during reline, improvements in burden and fuels, installing second tapholes and increasing the wind, will increase the potential casting emissions from individual furnaces. The decrease in total number of blast furnaces, and the associated increase in productivity per furnace, coupled with the industry's research of new control techniques, has resulted in a crucial economic turn-around in the cost of controls per ton of hot metal.

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EFFICIENT AND ECONOMICAL DUST CONTROL SYSTEM FOR ELECTRIC ARC FURNACE

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ABSTRACT

The total efficiency of a dust control system is a product of collecting and filtering efficiencies. Most of existing dust control systems for electrical arc furnaces have inefficient collecting and very efficient filtering components. The poor efficiency of collecting hoods is a result of their distance from the source, existing cross wind in the melt shop and lack of sufficient exhaust capacity even at very high gas flow rate.

The only rational and economic solution is to capture the fumes at or close to the source. The system installed in Sidbec-Dosco Contrecoeur melt shop is employing retractable collecting hoods located close to the ladle. It achieves high collecting efficiency at low exhaust rate of gas flow without interference with operation of the overhead crane.

The paper in question provides technical and economical analysis of several alternative solutions of dust collecting system for electric arc furnaces in steel making plants.

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EFFICIENT AND ECONOMICAL DUST CONTROL SYSTEM FOR ELECTRIC ARC FURNACE

During its operating cycle the modern high powered electric arc furnace releases about 1% of the weight of the molten steel as fume and dust.

This emission contains a variety of metal oxides including heavy metals.

For health reasons of the workers employed in the melt shop and the general population living around the plant, the emissions must be limited to a degree balanced between the cost of control and social benefits resulting from this control.

At the present time legislature and regulations in North America and Europe require that approximately 94 to 96% of all emissions from the electric arc furnace operation are to be captured. Only 4 to 6% can be allowed to exit to the atmosphere.

There are also health regulations in force, which limit the dust concentration inside the plant.

The task of the project engineer is to provide control systems which will satisfy the regulations at minimum investment and operational costs.

In order to find the best solution, it is necessary to quantify the emissions from the furnace for each phase of the operating cycle. The average of data obtained are shown in table # 1.

ACTION:	WEIGHT OF NON CONTROLLED EMISSION	TIME OF DURATION OF EMISSION
	KG / TONNE	IN MINUTES
INSPECTION AND FETTLING	0.06	3 TO 20
CHARGING	0.24	1.5 TO 3
MELTING AND REFINING	9.25	120 TO 150
TAPPING AND DEOXIDIZING	0.40	5 TO 11
SLAGGING	0.05	3 TO 5
TOTAL EMISSION	10.0 KG / TONNE OF MOLTEN STEEL	

TABLE 1 WEIGHT AND DURATION OF DUST EMISSION

A survey of available data shows a large spread of specific weight of uncontrolled emissions ranging from 6 to 24 kg per tonne of molten steel.

The factors influencing the high rate of particulate emission are shown in table # 2.

OILY SCRAP
LIGHT GAUGE SCRAP
PAINTED SCRAP
ZINC COATED SCRAP
PNEUMATIC FEED OF LIME AND DOLOMITE
MORE THAN ONE BUCKET CHARGE
DOORS OF THE FURNACE OPEN
LEAKY LINTEL AROUND THE ROOF OF THE FURNACE
WORN OUT REFRACTORY REQUIRING REPAIR
ACCIDENTS LIKE: BROKEN ELECTRODES
INTERRUPTION OF POWER SUPPLY

TABLE 2 - FACTORS INCREASING THE PARTICULATE EMISSIONS OF FUME AND DUST FROM THE ELECTRICAL ARC FURNACE

Beside the particulate emission there is also an emission of gasses: carbon dioxide CO_2, carbon monoxide CO, nitrogen oxides NO_x, hydrogen H_2, water vapour H_2O and a vast variety of hydrocarbons and other inorganic and organic compounds.

Of particular interest for the project engineer are emissions of combustible gasses since they may cause explotions. In order to reduce teh chances of such an accident, additional air, necessary for combustion, is introduced into the ducts, and appropriate dilution is added to remove the mixture of gasses and air from the explosive range.

Another cause of explosions is: closed vessels containing gasses and liquids, for instance: hydraulic cylinders, pumps and valves. They burst during heating, suddenly releasing their content, which expands, or ignites instantly. In winter months, there is a danger of explosion by ice frozen into crevices of the scrap. Contact of water and molten metal dissociates water into hydrogen and oxygen which recombine again with explosive force.

The rate of particulate and gasous emissions varies in a wide range during the cycle of operation of the electric arc furnace.

The total efficiency of a dust control system is a product of collecting and filtering efficiencies. Most of existing dust control systems for electrical arc furnaces have inefficient collecting and very efficient filtering components. The poor efficiency of collecting hoods is a result of their distance from the source, existing cross wind in the melt shop and lack of sufficient exhaust capacity even at very high gas flow rate.

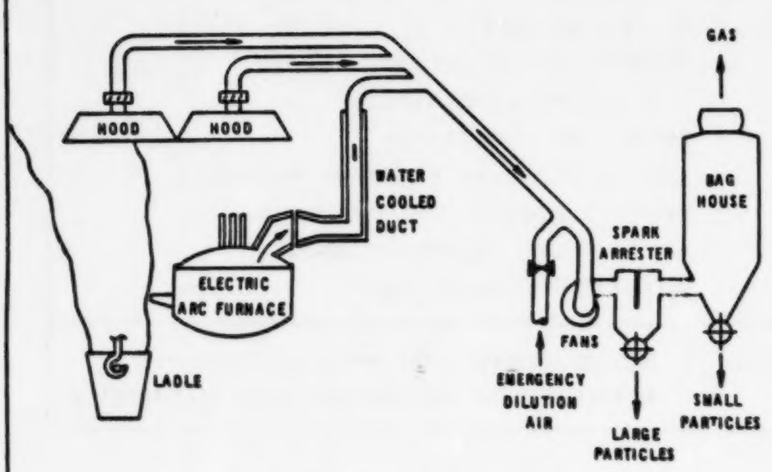

FIGURE 1 : CONVENTIONAL DUST CONTROL SYSTEM

The new cycle of operation begins with inspection of the refractory. The electrodes and the roof are raised and moved off the furnace. Since the furnace is nearly empty, there is very little particulate emission. If the refractory needs repair, a procedure called fettling is performed. A plastic refractory is blown, or thrown by centrifugal pump toward the places needing repair. The moisture of the plastic refractory evaporates quickly and takes some of the refractory into a column of raising vapour. This first emission is partially captured by an exhaust hood located at the roof truss level in the charging bay. The second part of the emission falls down mostly along the walls of the building. The third part exits by the roof ventilation into the ambient atmosphere.

When the refractory of the furnace is in good condition, there is no need for inspection and fettling. The cycle begins with charging: the roof of the furnace is opened, the charging bucket filled with scrap carried by the overhead crane arrives, centers with the axis of the electric arc furnace and releases its load into the furnace. In order to save wear of the refractory at the bottom of the furnace the charging bucket is loaded first with light scrap, and next, with heavy scrap. Light scrap has a large surface to volume ratio, and is more contaminated than heavy scrap. The sudden contact of the light scrap with hot refractory heats the thin scrap layer rapidly, evaporating water first, and hydrocarbons (oil, plastics, rubber) second. The vapours of hydrocarbons ignite within few seconds.

The intensity of the flame depends on the hydrocarbon content in the scrap. Shavings contain up to 5% of oil by weight. Large amounts of oily scrap in the charge may result in flames up to 20 meter high reaching the roof of the building. In these conditions, gas emissions rate may be more than 15 m^3/sec. for each square meter of the furnace hearth area. With limited content of oily scrap in the charging bucket the gas emission rate is about 5 m^3/sec. for each square meter of furnace hearth horizontal projection.

The total charging operation can be performed by skilled operators in less than 90 seconds. The large volume of gas and fume released is normally beyond the capturing capacity of the exhaust system located over the furnace.

The result is a visible emission escaping by the melt shop roof ventilators into the atmosphere.

After charging the melting opeartion begins. Three electrodes are lowered into the furnace and electric power is applied gradually until full power is reached. The cold scrap is therefore heated simultaneously from outside by the walls, bottom and roof of the furnace and from inside, by radiant heat developped by the electric arc. The process of: vaporization melting and sublimation reaches throughout the total scrap mass. Since the temperature in different parts of the charge is not uniform, a mixture of vapours and gasses escapes from the furnace.

In the present state of technology, the common method used to capture emissions issued during the melting process is direct evacuation. This is done by applying sufficient suction at the 4th hole (3 holes for electrodes) in the roof of the furnace. The practice shows, that the exhaust rate of 0.14 kg/sec. of gas for each Megawatt of the main transformer rating is sufficient for normal conditions. Since the temperature of the gaseous emissions rises up to 1875°C during the melting period the gasses are cooled first in a water cooled duct reaching the roof of the melt shop and diluted to provide 100% of excess air for combustion of CO and H_2 and later diluted for protection of the ducts with air drawn from the hoods located over the furnace.

In some installations, an additional cooling of gasses is performed in a radiant cooled consisting of a series of tubes exposed to the ambient air.

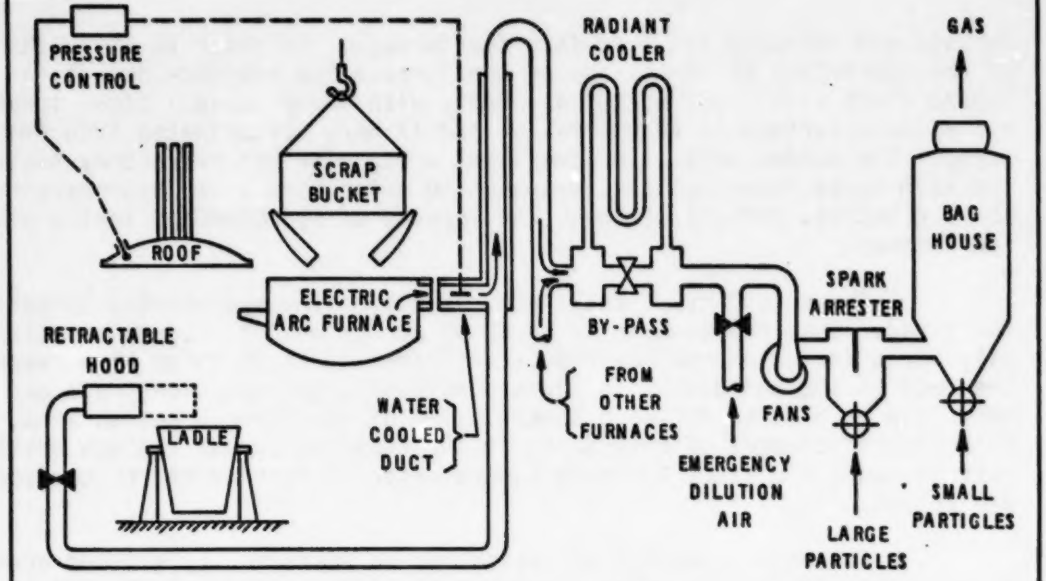

FIGURE 2 : ELECTRIC ARC FURNACE ECONOMY DUST CONTROL SYSTEM SCHEMATIC (WHEN CHARGING)

The gas dilution factor is about 8. It means that about 1.12 kg/sec. of gas and air per each Megawatt of the furnaces main transformer rating reaches the dust collector, which is normally a bag house. The temperature in the baghouse should not exceed 135°C for Dacron bags. New materials for bags allow for higher operating temperature, which in turn reduces the quantity of dilution air, power drawn by fans, dimensions and cost of installation.

The gas pressure in the furnace should be kept slightly negative for the melting of carbon steel and slightly positive for the melting of alloy steels.

This control of pressure is necessary to avoid excess infiltration of ambient air into the furnace since the excess air increases burn out of the electrodes, increases emissions and increases electric power consumption. The positive pressure in the furnace results in emission around electrode holes in the roof. The fugitive emissions can be captured by the hood over the furnace but at the cost of drawing a large quantity of infiltrated ambient air into the column of rising gas.

The gas velocity in the ducts carrying dust is set at 15 m/sec. for each meter of duct diameter, and shall not be less than 15 m/sec. for small dia. ducts. The common operating problems with direct evacuation systems are: burning of holes in the bags by incandescent material, build-up of cake on the bag surface, erosion of fan blades and occasional explosions.

Due to the short gas transfer time from the furnace to the baghouse (about 5 to 9 seconds) some incandescent particles may reach the bags resulting in a burning of holes. In order to avoid the transfer of large particles, a cyclone or a plenum chamber with reduced gas velocity should be provided to eliminate particles larger than 0.5 mm of diameter.

Build-up of cake on the bags is a result of excessive moisture content in the gas at the start of the operation and of moisture entering the baghouse after the end of the operation. The captured dust contains large amounts of burnt lime, which remains as a fine, submicron size, powder when it is dry. In the presence of moisture this burnt lime becomes a mortar and clogs the fine passages between the yarns of the woven fabric of the bags. Shaking or back flow of gas used as a means to clean up the bags may be not fully effective to dislodge this mortar.

In time the layer of mortar builds and the resistance to the flow of gasses increases. The stresses due to increased pressure may rupture the bags. Keeping the bags dry between operations by applying external heating seems to be too expensive, but operation of the direct evacuation system for a half an hour after stopping of operation will dislodge most of the lime from the bags, thus at least partially preventing the cake build-up.

In the Sidbec-Dosco steel making practice, when the first charge is partially melted, an addition of continuously fed pre-reduced iron pellets begins. The rate of feed is adjusted to the quantity of the electrical power supplied to the electrodes in order to maintain constant temperature of the molten bath. Burnt lime and/or dolomite and alloys are fed with pre-reduced pellets, into the furnace from the bins located on the roof of the melt shop. All continuously fed materials enter through a stainless tube through the 5th hole in the roof of the furnace. The downward motion of the falling material creates movement of the air in the feeding duct directed toward the furnace. An opposite movement of the hot gas from the furnace counteracts this movement of air. As a result of these two actions, an escape of gas from the furnace through the feeding duct is observed.

The emission through the feeding pipe can be controlled by reducing its diameter, and by applying suction at the funnel where the stationary and movable parts of the feeding pipe join.

In electric arc melt shops which do not employ continuous feed of pre-reduced pellets, an additional one, or more, bucket charges are used. The second and following charges of scrap fall into already molten metal, therefore, the instant burst of gasses is more violent than at the first charge. In order to reduce those violent emissions, the second and consecutive charges should consist of clean scrap.

Tapping into the ladle begins when the charge is melted, the furnace is deslagged, and the batch brought to the desired temperature and chemical content.

The tapping ladle may be suspended on the hoods of the overhead crane, or may be stationary, positioned on a stand located in front of the spout of the electric arc furnace.

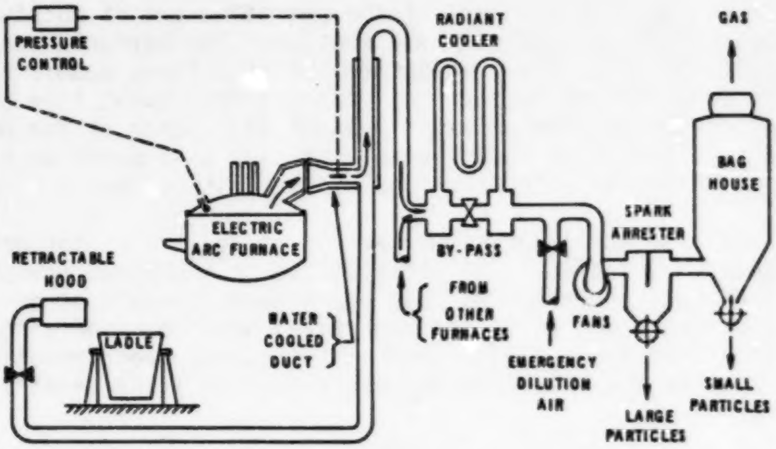

FIGURE 3 : ELECTRIC ARC FURNACE ECONOMY DUST CONTROL SYSTEM SCHEMATIC (WHEN MELTING)

The suspended ladle enables the falling height of the molten steel to be minimized, therefore, reduces generation of oxide fumes. However, this practice uses valuable time of the overhead crane, and makes confinement of escaping emissions more difficult. The stationary ladle, being fixed in place, provides the possibility to collect the fumes through the hood which is close to the ladle. This is far more efficient than by the hood located at the roof truss level of the melt shop, normally used for the suspended ladle fume control. Direct measurements of the rate of emissions during the tapping operation in Sidbec-Dosco, Contrecoeur Melt Shop revealed that the gas emission for each square meter of the ladle's horizontal projection area is 3.5 m^3/sec. at the ladle rim level, and 40 m^3/sec. at the roof truss level. This is due to entrapment of the ambient air by the column of highly turbulent gasses rising from the ladle.

The hot gas column starting from the ladle is deflected by horizontal air currents in the casting bay of the melt shop. Deflection up to 45^o were observed in some cases. These were not constant, being influenced by changes of wind velocity and direction, the opening of doors and by activating the on/off switches of the preheating furnaces for the ladles.

In these conditions, if the evacuation hood system located on the roof truss level was selected its capacity would be about 450 m^3/sec. (950,000 ACFM) to obtain an average of 85% dust capturing efficiency (for tapping).

The estimated cost in 1977 for this type of dust control system of this capacity was 6.5 to 8 million U.S. dollars.

In order to save investment and operating costs and to achieve better fume control during the tapping operation, an idea was developped to use the existing capacity of the direct evacuation system, which remains idle during tapping time.

A swinging hood located just over the stationary ladle was designed. This hood has a cut-out permitting passage of the stream of molten metal pouring from the spout of the electric furnace.

The ladle hood would have been suspended on a structure which would pivot and rotate to permit access of the hoods of the overhead crane to the trunnions of the ladle when the ladle was filled with molten steel.

There was an opinion that a swinging hood over the ladle could be easily damaged, and would take too much valuable space in the casting bay of the melt shop.

A new design was prepared: a horizontal retractable hood with a blanket of horizontal air currents created by fans located opposite to the intake of the hood. All mechanisms were located under the tower supporting the additive bins. Being hidden under the structure of the tower the mechanisms were safe from accidental striking by the hooks of the overhead crane and no additional space was required in the casting bay.

A prototype was made and installed for one of the furnaces. The tests showed that fans pushing the air were not required and the ladle fume evacuation system could collect about 85% of the fumes issued during tapping operation.

The success of the prototype was followed by installation of similar units for all four furnaces in the Contrecoeur Melt Shop.

The total cost of four ladle fume control systems was $500,000 which is much less than 6.5 to 8 million dollar estimate for an evacuation system with similar efficiency comprising hoods located at the roof truss level.

Retractable hoods work in automatic or manual mode. If automatic mode is selected then the signal from the tilting furnace actuates the extension of the hood toward the ladle and simultaneously closes the damper of the direct evacuation system and opens the damper of the ladle fume evacuation system. When, after filling the ladle the furnace returns to its vertical position another signal causes retracting of the hood and reversal of the position of the dampers.

Figure # 4 shows a schematic of the combined system.

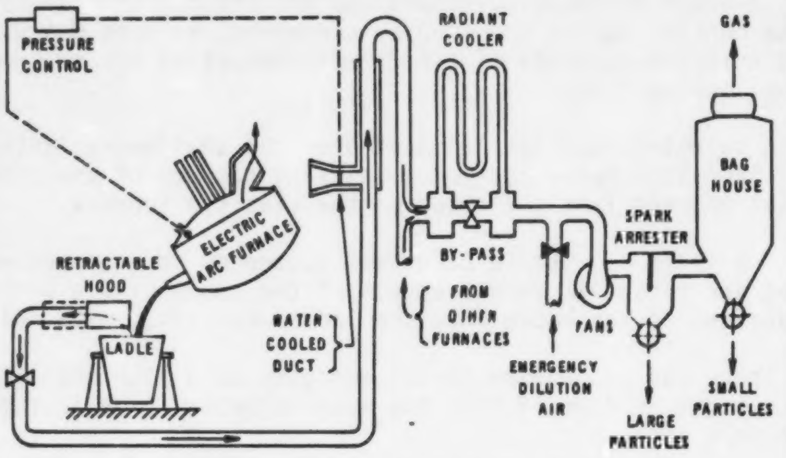

FIGURE 4 : ELECTRIC ARC FURNACE DUST CONTROL SYSTEM SCHEMATIC (WHEN TAPPING)

At the present time in our Contrecoeur Melt Shop two major sources of air pollution from the operation of the electric arc furnaces are under control: emissions when melting and refining, and when tapping. A third, however much smaller emission, when charging, requires about 200 m^3/sec. exhaust capacity in a hood located above the furnace at the roof truss level.

Experimental work is being committed to develop an improved method of controlling emission during operations of charging, inspection and fettling.

Development of an efficient and economical fume and dust control system for electric arc furnaces have been done in an existing operating Melt Shop. Valuable information has been gathered concerning: engineering, operational, maintenance and human relation factors.

Some of these observations are shared here.

For an existing melt shop with multiple electric arc furnaces the most economical solution of fume and dust control is the full utilization of capacity and time of an existing direct evacuation system, in order to control emissions during melting, tapping and charging periods.

There should be a centralized manual or automatic dispatch directing necessary flow rate for different emission sources in order to obtain the best total dust collecting efficiency at a minimum cost.

At the present time there are no integrating instruments available on the market which can provide a signal proportional to dust mass transfer rates in different ducts of a complex integrated dust collecting system. Such signals could be processed in a real time computer to open the dampers of the ducts carrying the dust, and close dampers on ducts which momentarily carry little or no dust at all.

Manual operation of dust control systems calls for continuous attention sound judgement and quick response and requires additional personnel.

On the basis of observations made of the operation of many steel melt shops, one can say that the dust control equipment can be easily damaged by the build-up of slag, overheating, clogging by dust and mechanical abuse. Therefore, it has to be continuously supervised by trained personnel in order to ensure its availability all the time.

Since production always has maintenance priority even a well designed dust control system left without sufficient supervision and proper care for long period of time, becomes quite often inoperative resulting in excessive emissions into the atmosphere and excessive dust concentration in the working area.

When a "green-field" installation of an electric arc melt shop is in the preliminary planning stage, a total enclosure over the furnace and ladle could be an alternative solution. However, in an existing melt shop, there is rarely a chance of implementing this idea, due to space limitations. In addition, the possibility of frequent damage to the doors of the furnace envelope is a factor which restrains the acceptability of total enclosure of an electric arc furnace.

In summary, one can say the present trend in the design of dust control systems for electric arc furnaces is to utilize a minimum of exhaust capacity, but to use it fully in all stages of the operating cycle.

Since the dust collecting hoods located close to the dust source are nearly ten times more efficient than the hoods located on the roof truss level, their high collecting efficiency reduces the necessary exhaust gas flow rate and associated cost of investment and operation of a dust control system. For this reason, one can expect that in the future design of dust control systems, the systems with hoods close to dust source will be employed more frequently.

ACKNOWLEDGMENT

The statistical data re emissions were compiled from reports of Environment Canada APCD subcommittee electric arc furnace headed by Mr. V.C. Havelock in 1977.

The measurements of gas flow rate when tapping and charging were made by Mr. M. Bender of Hatch & Associates, Toronto.

The design and development of retractable hood for tapping was done by Sidbec-Dosco engineering group headed by Mr. R. Sevigny.

The practical implementation of the idea of close to dust source exhaust system was encouraged by Messrs: T.E. Dancy, senior vice-president of technical studies and development and G.H. Laferriere, director of engineering.

IRON AND STEEL INHALABLE PARTICULATE MATTER SAMPLING PROGRAM: AN OVERVIEW PROGRESS REPORT

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Iron and Steel Inhalable Particulate Matter Sampling Program
An Overview Progress Report

Abstract

EPA's Office of Research and Development has entered into a major program to develop inhalable particulate matter (IPM) emission factors, where IPM is defined as airborne particles of $\leq 15\ \mu m$ aerodynamic equivalent diameter. The Metallurgical Processes Branch of EPA's IERL-RTP is responsible for the iron and steel industry segment of this program. This paper presents a summary of efforts to date. Implementation has proceeded along two major lines of action. The first follows the classical route: literature review, prioritization of sources, identification of sources for which existing data are adequate, selection of plants, testing, and finally reporting results. The other aspect consists of meshing the IPM requirements with those of other EPA sampling programs, thus reducing overall cost to EPA and minimizing inconvenience to the host plants.

A review of existing particle size data showed not only that relatively little data exists, but also that most existing data are of questionable quality. Therefore, the field test program entails sampling virtually all significant sources. To date, tests have been completed of basic oxygen furnace (BOF) charging and tapping, hot metal desulfurization, blast furnace cast house (building evacuation approach), uncontrolled paved and unpaved roads, and BOF main stack (limited combustion system after scrubber). Discussions are now underway with several plants to test other high priority sources. It is anticipated that funds will allow duplicate tests at another plant of at least the highest priority sources.

INTRODUCTION

The U.S. Environmental Protection Agency is required, under the amended Clean Air Act of 1977, to review the scientific basis for the total suspended particulate ambient air quality standard. Major consideration is being given to a size-specific particulate standard focusing on inhalable particulate matter (IPM), defined as airborne particles of $\leq 15\ \mu m$ aerodynamic equivalent diameter.(1) EPA has initiated an extensive program to compile and review existing data and, where necessary, conduct field sampling programs from which reliable emission factors can then be determined. These emission factors will be available to the States for the purpose of revising State Implementation Plans if an ambient standard based on particle size is promulgated.

EPA's Office of Research and Development is responsible for developing these IPM emission factors. A major part of this effort is directed toward the steel industry. This paper discusses briefly the rationale behind the selection of $15\ \mu m$ as the upper cut point in the IPM definition and why a field sampling program must be undertaken. Sampling protocols are described for ducted condensible and noncondensible emissions and for fugitive emissions. The rationale and approach being followed to select test sites are also discussed. Results obtained to date are summarized and conceptual plans for the remainder of the program are presented.

DISCUSSION

The human respiratory tract consists of three main areas:(1) the upper respiratory tract, conducting airways, and gas-exchange area. All available data demonstrate that direct health effects from particles $\geq 15\ \mu m$ are primarily restricted to the upper respiratory tract. IPM is the term used to represent airborne particles capable of affecting the lower respiratory tract which includes the last two of the three general areas. Thus the definition of IPM has been taken to mean those particles of $\leq 15\ \mu m$ aerodynamic equivalent diameter. Although discussion continues among health effects experts as to the specific upper cut point for an ambient air particulate standard based on size, the definition of IPM remains unchanged. A secondary cut point of $\leq 2.5\ \mu m$ has been recommended to estimate that fraction of particles capable of penetrating to the gas exchange area of the respiratory system. Sampling data generated under this program will include several intermediate cut points to enable accurate interpolation once an ambient air standard cut point is selected.

Sampling Protocols

Sampling protocols have been developed to permit IPM measurement of ducted(2,3,4) and fugitive(5) emissons.

Ducted Sources (Non-Condensible Emissions) - Initially, EPA felt that the main interest lay in determining total IPM of $\leq 15\ \mu m$ and also the quantity of IPM $\leq 2.5\ \mu m$. Since existing cascade impactors are limited both by small sample collection capability (hence very short sampling time in heavily loaded streams) and in collecting particles >10 μm without particle "bounce," EPA decided to develop a sampling system specifically for the IPM program.

The result of this effort, depicted in Figure 1, consists of two in-series cyclones inserted directly into the stack using a modified EPA Method 5 probe and associated equipment(6). Operating at a nominal flowrate of 23 l/min, the large cyclone has a D_{50} of 15 μm and the small one, 2.5 μm. The filter (not shown) collects all particles <2.5 μm which, when added to the small cyclone catch, equals total IPM. A significant advantage is the capability to collect a fairly large sample, which means a longer sampling time.

During this development program it was found that the button hook nozzle commonly used with cascade impactors was, by itself, a very effective collector of particles <15 μm. Thus an important criterion for any particle sizing device is that it have a straight nozzle. A comparison was run between the so called IPM train described above, an Andersen 2000 Mark III in-stack cascade impacter equipped with a 15 μm cyclone precutter, and an Andersen in-stack high capacity stack sampler (HCSS). As reported earlier, in the paper by J. Steiner and D. Bodnaruk(7), test results showed that all three devices gave comparable results.

Subsequent to the development of the IPM train, controversy occurred concerning the selection of the upper cut point for the purpose of defining a particle size ambient particulate standard. Consequently, the decision was made to use the in-stack cascade impactor with a 15 μm cyclone precutter (see Figure 2). The data thus generated would permit the more accurate plotting of curves relating particle size versus cumulative sample weight emitted per unit process weight. A straight nozzle would, of course, be used in all tests. The field test protocol requires four measurements each for particulate mass concentration and for particle size distribution. The impactor data yield the size distribution which is then applied to the mass measurement to give cumulative emission factors as a function of particle size. An EPA Method 5 sampling train is used for the mass measurement.

Ducted Sources (Condensible Emissions) - Some iron and steel process emissions contain a significant fraction of condensible compounds. In this case, significant is taken to mean greater than 10 percent of the total particulate emitted. Typical sources in this category are: coke oven charging, quenching, and battery stacks; sinter windboxes; and electric arc furnaces. The condensible fraction may contain both organic and inorganic compounds.

The condensible emission IPM sampling protocol was prepared by Southern Research Institute, under contract to the EPA. The general approach is to introduce a slip stream of the source exhaust into a dilution chamber supplied with clean ambient air. The dilution air flowrate may be on the order of 10-30 times the slip stream flowrate. Total particulate and particle size samples of the diluted slip stream are obtained after complete mixing. The samples thus collected would reflect their initial state in the atmosphere.

The condensible sampling system has been designed and units are now being fabricated. As shown in Figure 3, its essential parts include a dilution chamber approximately 30.5 cm in diameter and 183 cm long. An ID fan supplies filtered air to one end of the chamber. The source slip stream is extracted isokinetically using a heated probe and is introduced at the same end. At the outlet end of the chamber a high volume impactor filter assembly collects and sizes the total particulate.

Fugitive Sources - The measurement of fugitive particulate emissions by size requires several sampling devices. A standard high volume sampler gives total suspended particulate (TSP); a high volume sampler (with a size-selective head) and a cascade impactor on a high volume sampler (with a horizontal elutriator as a 15 μm precutter) both yield particle size data. One major reason for using multiple particle sizing devices at this time is the lack of experience upon which to base the selection of a better device. As field experience accumulates, a decision can be made, thus reducing both testing and analytical costs.

A typical upwind/downwind fugitive emission field setup, such as for measuring emissions from vehicular traffic on a road, would include:

(1) selection of a section of road which was normal to the wind direction and sufficiently remote from buildings, trees, or other roads to avoid interference;

(2) a sampling array on the upstream side of the road consisting of three high volume samplers -- one equipped for TSP, one with a size-selective head, and one with a cascade impactor, all situated 1 m above ground surface;

(3) an array at the downwind site consisting of the same equipment as upstream at a 1 m height, plus two high volume units at a 2 m height -- one with a size-selective head, the other with a cascade impactor, and all five units located on the plume center line;

(4) a size-selective high volume sampler at each plume wing at a 1 m height; and

(5) for determining verticle profiles, locate high volume samplers with elutriators on the plume centerline at heights of 1, 2, 3, and 4 m.

The quasistack method involves hooding the fugitive emission source and drawing off emissions through a duct; emission measurements would then follow the ducted emission protocol. Obviously, this approach would only be feasible for relatively small or compact sources since the expense of building hoods and ducts just for test purposes could be prohibitively expensive. Alternatively, if a normally fugitive source, such as BOF charging, is found to be well contained at a plant, then every effort would be made to perform tests at that plant assuming it was representative of the industry in its operational characteristics.

For the measurement of fugitive emissions exiting through a roof monitor, either a high volume cascade impactor fitted with the elutriator head or a fugitive assessment sampling train (FAST) would be used. The FAST shown in Figure 4 offers the advantage of collecting large quantities of material in selected size fractions, permitting subsequent chemical and biological characterization.

Source Selection

At the outset of the iron and steel sampling program, the decision was made to proceed with field test selection voluntarily, rather than through the application of Clean Air Act Art. 114. Industry contact was initiated through the American Iron and Steel Institute (AISI) who established an ad hoc coordinating committee. Meetings with this committee were held to present an overview of the whole program and, following resolution of outstanding issues, to review sources selected for testing.

The EPA/AISI cooperative effort has thus far resulted in the mounting of an extensive field sampling program at Armco, Inc.'s Middletown Works. Discussions will soon be initiated with several other companies; several field test programs should be getting underway soon.

The source selection priority list, shown in Table 1, was developed based on estimated controlled particulate emissions from each source on a nationwide basis. This prioritization represents an average of emission factors developed under separate efforts: one represented very good control efficiency(8); the other, a somewhat lower level which might be termed typical for non-new installations(9). It is only fair to say that, at best, this procedure is still rather arbitrary but does nevertheless provide a rational approach to source selection.

The source selection priority list also considers existing particle size data and its quality. Since there is very little particle size data for iron and steel sources, this consideration did not affect the priority position of any source. Six data sets are currently contained in EPA's Fine Particle Emissions Information System (FPEIS)[10]. These data sets, consisting of three open hearth stack tests, two electric arc furnace tests, and one coke pushing shed test, are summarized in Figures 5-7, respectively. Although these data are judged to be good, consideration must be given to when they were obtained (1974-77) and the advancements made in particle size sampling technology since then. These three sources should be tested again.

In addition to the selection procedure coordinated with AISI, every effort has been made to combine measurement of IPM with other EPA sampling programs. Not only does this serve to reduce EPA expenditures, it also reduces inconvenience to the host companies. To date, these "piggy back" projects constitute the greatest area of activity due primarily to the fact that initial ground work had already been laid by the Agency, making it possible to mount the field effort relatively quickly.

Results To Date

Kaiser Steel Corp. The first two sources tested under the IPM program were the hot metal desulfurization (HMDS) and BOF charging and tapping emission control systems recently installed at Kaiser Steel Corporation's Fontana, CA plant. These tests, performed in coordination with EPA's Office of Enforcement through the Region V office, consisted of total particulate by EPA Method 5 and particle size before and after the control device which was, in both cases, a baghouse. EPA's contractor was Acurex Corporation.

Particle size before control was measured with the EPA two-cyclone IPM train described previously. Due to the low particulate concentration, baghouse outlet particle size in both cases was measured with an Andersen Mark III impactor fitted with the 15 μm cut point cyclone precutter.

BOF emissions from hot metal charging and tapping of finished steel were measured separately. Charging measurements did not include the addition of scrap. Results of the HMDS tests were reported in detail earlier in this Symposium.(7)

Armco, Inc., Middletown. The extensive testing program undertaken for EPA by Midwest Research Institute at Armco, Inc.'s Middletown Plant encompassed both open sources and ducted sources; emphasis was on the former. Specifically, emissions from paved and unpaved roads were measured before and after the initiation of emission reduction schemes. For paved roads, the emission reduction consisted of flushing with water and/or sweeping -- vacuuming at regular intervals. Berms of paved roads were treated with Coherex®. The controlled unpaved road was first tested shortly after application of the suppressant (Coherex®) and again several weeks later to establish the emission control efficiency decay curve.

In addition to the road tests, measurements were made of windblown emissions from the coal pile and emissions arising as a result of coal pile maintenance.

All of these open source measurements were made using the upwind/downwind techniques. Road surface silt content was sampled to allow correlation with the measured emission rate. Numerous samples were taken from other inplant roads to develop an idea of the representatives of the sampled road segments and also to allow a more realistic extrapolation of the test data to the whole plant.

Ducted emissions measured at Middletown were from the BOF main stack. Testing of the open hearth stack is being considered. Although the IP protocol calls for measurements before and after the control device, the nature of the limited combustion BOF operation precluded measurements before the scrubber. Measurements after the scrubber included total particulate and particle size as per the protocol. Results are being reduced and should be available in December 1980.

Testing of the open hearth stack is in the initial planning stage. It is intended that the field program consist of total particulate and particle size samples before and after the control device for each major portion of the furnace cycle. Each furnace at Middletown has its own control device.

Dominion Foundries and Steel Company. Dominion first installed cast house emissions controls several years ago. The No. 1 blast furnace cast house control system, installed in 1975, was tested by EPA(13) in 1976. This system employs the total building evacuation concept. Although particle size measurement of uncontrolled emissions was attempted, the data were not reliable due to particle bounce (no precutter was used). Using 1980 techniques which employ the 15 μm cyclone precutter ahead of the cascade impactor would have solved this problem. The combined control system for cast houses No. 2 and 3 was started up in November 1978. These cast houses share a common fan and baghouse and also employ total building evacuation. Cast house No. 4 is currently being used to evaluate concepts for local emission control.

The IPM emission tests are being run on the combined system serving No. 2 and 3; however, measurements are being made only when No. 3 is casting. Emission tests follow the protocol for ducted sources. Measurements are being made for EPA by GCA/Technology Divison in the duct upstream of the baghouse; no attempt is being made to measure the discharge from the open monitor on the baghouse. Testing will be completed in mid-November 1980; preliminary results are anticipated in January 1981.

Bethlehem Steel Corporation, Sparrows Point. GCA/Technology Division will be conducting emission tests for EPA at the new "L" furnace cast house at Sparrows Point later this month. This is a large modern furnace employing close-fitting hoods and covers over the trough, iron runners, and spouts, a practice pioneered in Japan. Emissions are ducted to a large baghouse. Emissions, following the ducted source protocol, will be measured in the duct upstream of the baghouse. Since this baghouse also controls emissions from numerous other fugitive sources, no attempt will be made to sample the open monitor discharge. Results of these tests are also anticipated early next year.

Future Tests

EPA is currently reviewing the overall status of the field testing program in light of the source priority list. Future tests will continue to address the highest priority sources first. Testing of high priority sources suspected of containing a significant fraction of condensible emissions (e.g., sinter plant windboxes, electric arc furnaces, and coke ovens) will be initiated as soon as the condensible emission sampling protocols are formalized and the necessary sampling equipment is available. In the meantime, noncondensible sources will continue to be tested as rapidly as possible.

ACKNOWLEDGEMENTS

The three sampling contractors for EPA's IP program are GCA/Technology Division, Midwest Research Institute, and Acurex Corporation. The AISI and its member companies (in particular Armco, Inc., Bethlehem Steel Corporation, Dominion Foundries and Steel, Ltd., and Kaiser Steel Corporation) have been most helpful.

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TABLE 1. IRON AND STEEL SOURCE PRIORITY RANKING FOR IPM STUDY, CONTROLLED EMISSIONS

Rank	Process	Industry total particulate emissions, Mg/yr
1	Coke quenching	34,500
2	Blast furnace cast house	22,700
3	BOF stack	20,000
4	Material stockpiles	16,300
5	Roadway travel	16,300
6	Coke combustion stack	16,300
7	BOF charge and tap	14,500
8	Coke pushing	8,900
9	Sinter, misc. fugitives	8,700
10	Sinter windbox	8,200
11	EAF charge, tap, slag	7,600
12	Coal preparation	7,400
13	OH stack	7,300
14	Coke door leaks	7,100
15	EAF stack	6,600
16	Sinter discharge end	5,700
17	Blast furnace top	3,700
18	Teeming	3.700
19	Ore Screening	3,300
20	BOF,misc. fugitives	2,200
21	Coke topside leaks	2,100

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TABLE 1. IRON AND STEEL SOURCE PRIORITY RANKING FOR IPM STUDY, CONTROLLED EMISSIONS (Continued)

Rank	Process	Industry total particulate emissions, Mg/yr
22	Reheat furnaces	2,000
23	Blast furnace combustion	2,000
24	OH roof monitor	2,000
25	Coal charging	1,800
26	Open area	1,100
27	Machine scarfing	670
28	BOF, hot metal transfer	650
29	OH, misc. fugitives	640
30	Soaking pits	570
31	EAF, misc. fugitives	540
32	OH, hot metal transfer	190

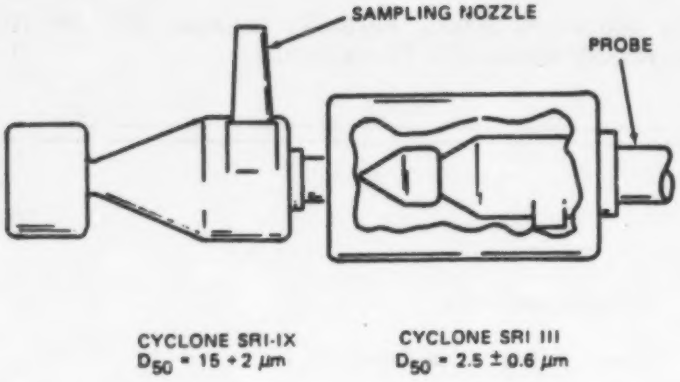

Figure 1.(2) Schematic of dual-cyclone sampler for inhalable particles.

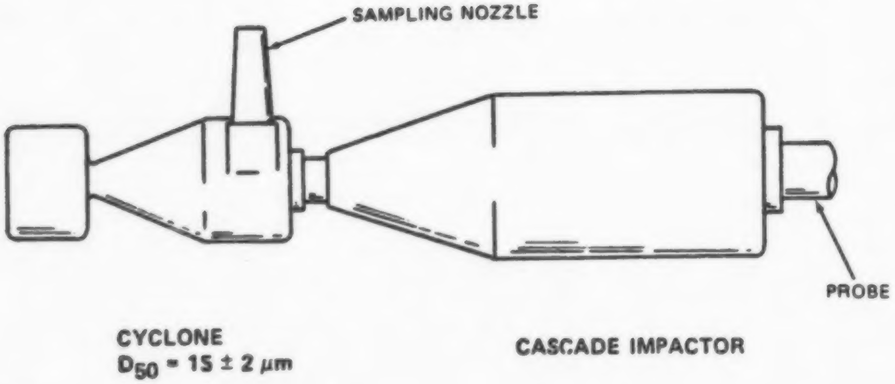

Figure 2.(2) Schematic of a cascade impactor/precollector cyclone system.

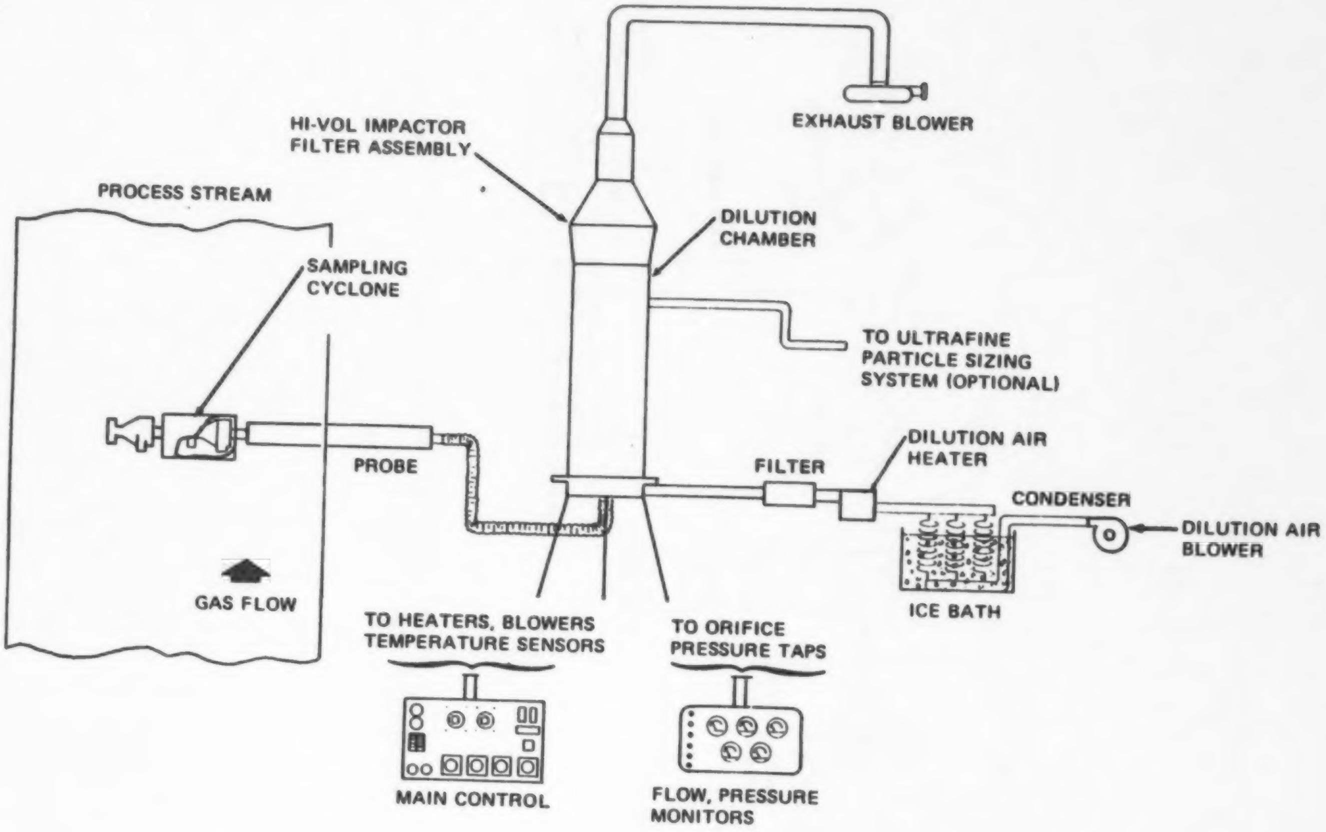

Figure 3.(4) Diagram of atmospheric dilution sampling system.

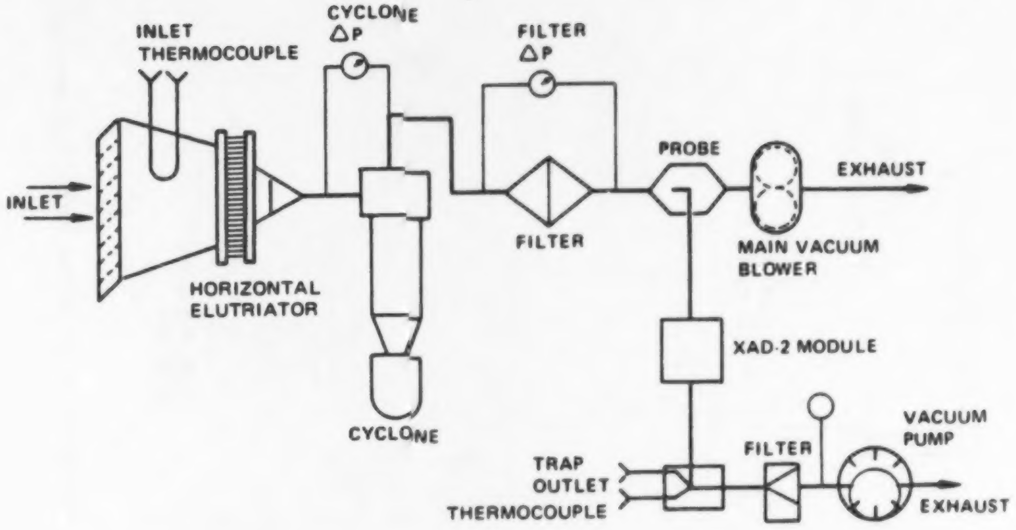

Figure 4. The FAST with a horizontal elutriator inlet for collecting inhalable particulate.

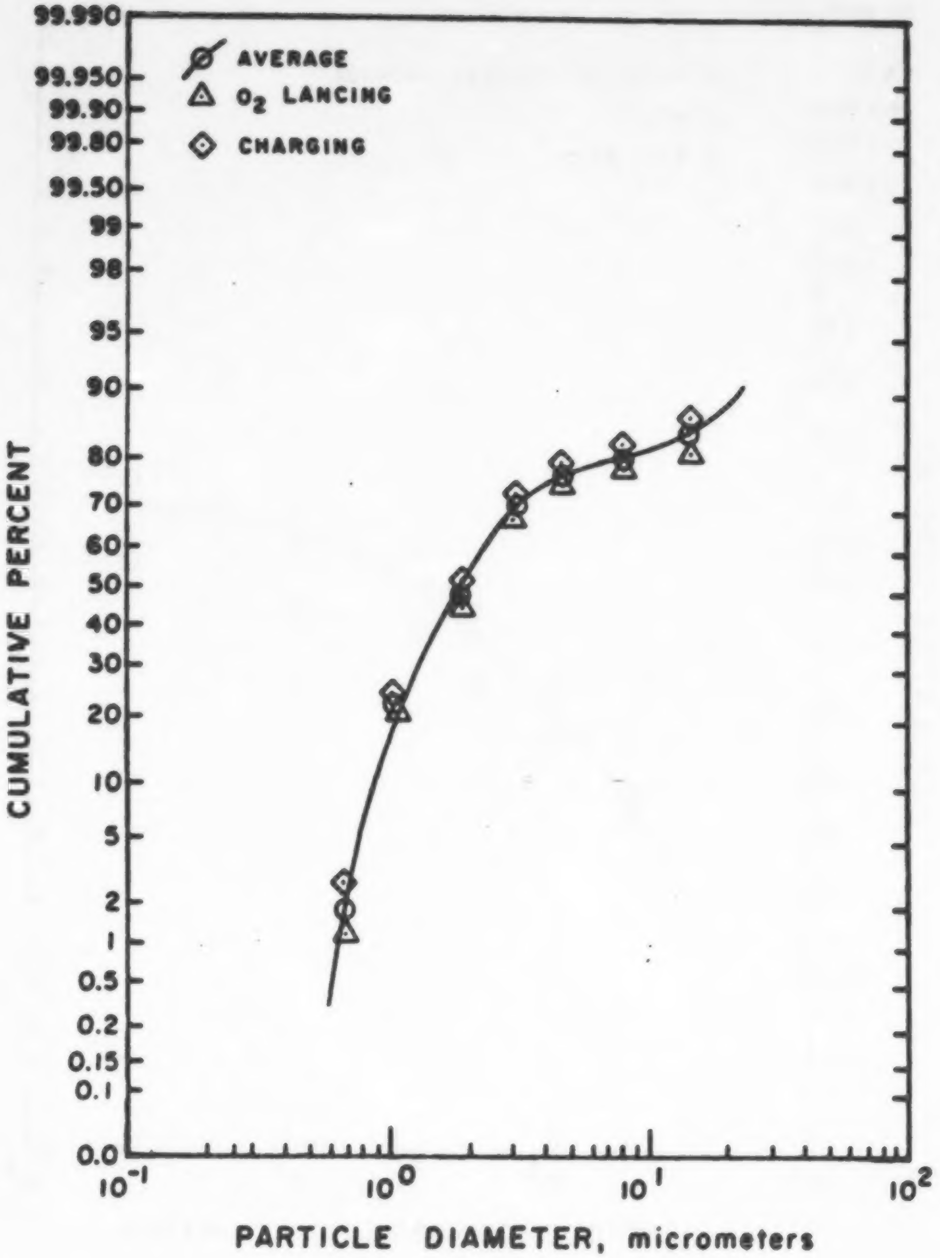

Figure 5.(11) Average size distribution - open hearth furnace emissions, uncontrolled.

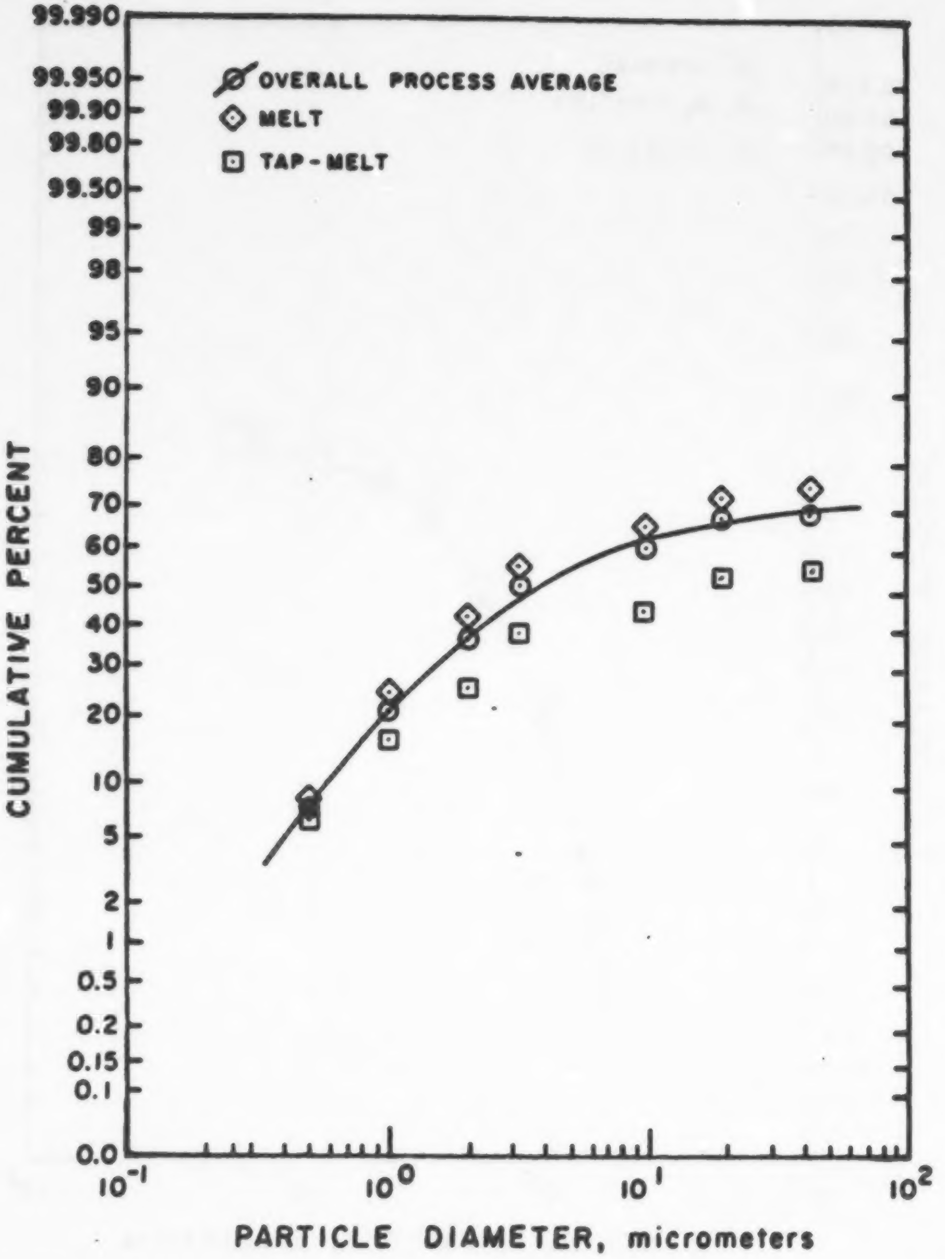

Figure 6.(11) Average size distribution - Marathom LeTourneau Electric arc facility.

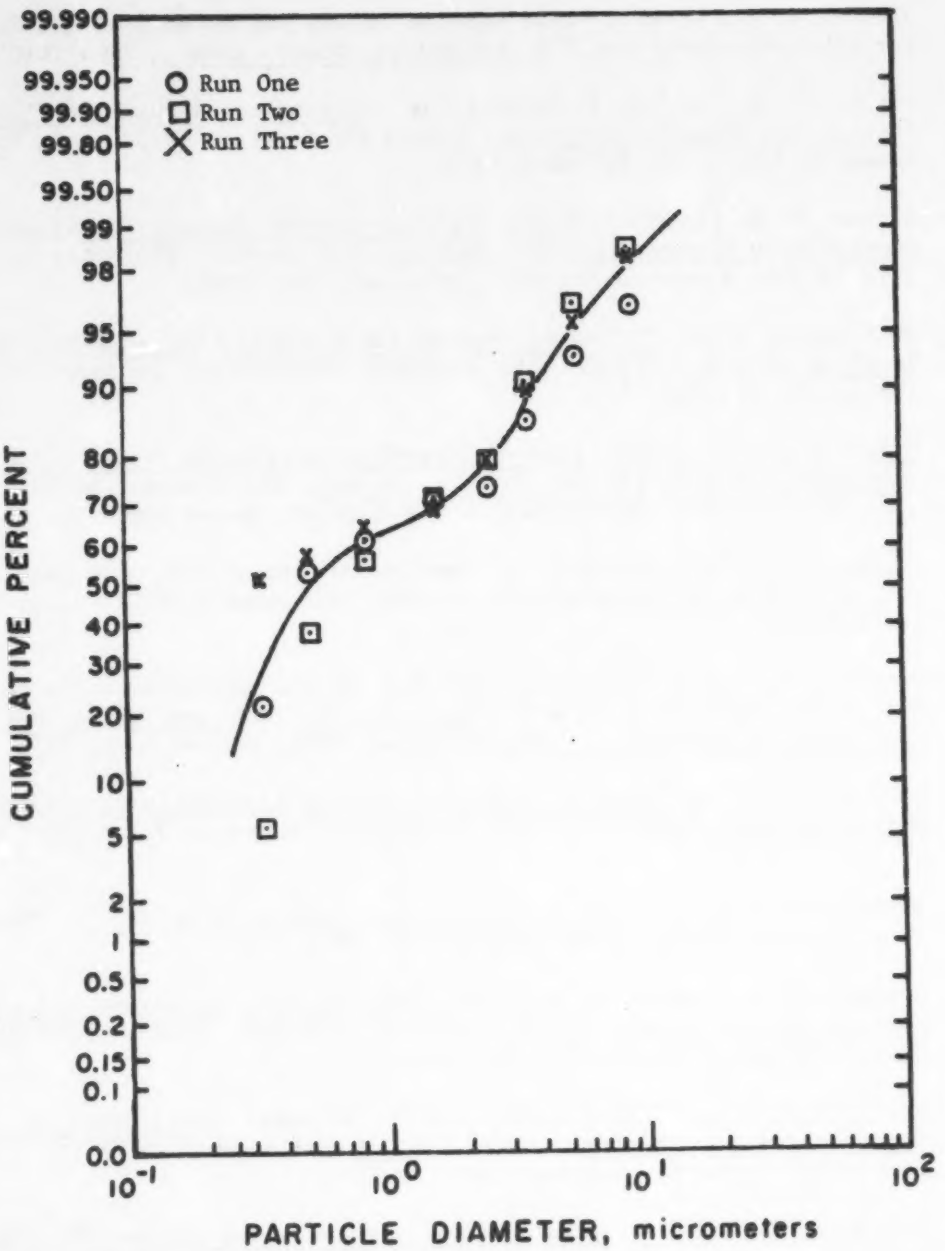

Figure 7.(12) Average particle size distribution--coke oven pushing.

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Session 2: WATER POLLUTION ABATEMENT

Chairman: George F. Haines, Jr.
Homer Research Laboratories
Bethlehem Steel Corporation
Bethlehem, PA

APPLYING GREENFIELD WATER SYSTEM DESIGN AND MANAGEMENT TECHNIQUES TO EXISTING STEEL PLANT FACILITIES

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HYDROTECHNIC CORPORATION

ABSTRACT

A great amount of emphasis is being placed on recycle, reuse, cascade, etc. systems for the purpose of reducing the amount of contaminants discharged from industrial facilities. These methods can and do reduce volumes of water and masses of contaminants discharged; however, the application of new principles to existing facilities is usually looked upon with, at best, extreme skepticism.

This attitude is understandable since, in many cases, an existing system cannot be completely or conveniently revamped to include all the "niceties" that can be designed into a greenfield site. A completely closed mind, however, cannot be tolerated in these days of increasing prices and stricter environmental controls. There is no room for the attitude of "we've been doing it that way for thirty years and no one can make us do it differently". Attitudes like that can only force management to spend much more money than is really needed to comply with the regulatory requirements for pollution control.

This paper presents various practices regarding the reuse, recycle and cascade of wastewater in steel plants which were either developed for greenfield installations and later applied to existing installations or those that were applied to existing installations directly. It also points out areas of difficulty which are encountered when existing facilities are upgraded. Design parameters must be carefully determined so that facilities are not grossly oversized or, more tragically, undersized. The treatment and reuse compatibility of one wastewater with another must also be ascertained so that incompatible "mixes" are not attempted.

Segregation of flows within existing mills, although initially costly in most cases, can be the most economic alternative. This is especially true when large quantities of "clean cooling water" combine with "dirty water". These various methods are presented together with descriptions of systems actually installed and operating to show the results that can be obtained with proper study and design principles.

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Due to the consideration of water pollution control, water conservation and the recovery of our precious resources, the recycle and reuse of water in industrial facilities is receiving a tremendous amount of attention. Various methods exist to effect reduction of discharges. These include in-process changes, close control of water chemistry, increased instrumentation, segregation of flows, etc. These methods can and do result in reduced volumes of water discharged and, in turn, the masses of contaminants discharged. However, the application of new principles to existing facilities is usually looked upon with, at best, extreme skepticism.

This attitude is understandable since, in many cases, an existing system cannot be completely or conveniently revamped to include all the "niceties" that can be designed into a greenfield site. A completely closed mind, however, cannot be tolerated in these days of increasing costs and stricter environmental regulations. There is no room for the attitude of "we've been doing it that way for thirty years and no one can make us do it differently". This type of attitude causes management to spend more money than is really needed to comply with the regulatory requirements while using undue amounts of energy.

Years ago when a new plant was designed the layout of the production facilities in a most practical manner was the prime consideration. This practical layout resulted in a smooth and efficient flow of raw materials to finished product. Little thought was given to water systems except to keep them "out of the way" and make sure they caused as few problems as possible. Scale pits and blast furnace thickeners were installed, not for the primary purpose of water pollution control but to safeguard against the clogging of sewers which could cause production delays and stoppages. As environmental regulations became stricter, clarifiers were installed after scale pits, portions of blast furnace gas washer water were recirculated, oils were skimmed and acids neutralized. Most wastewater collection systems "grew like Topsy" without overall plant or system-wide planning which resulted in mixes of different, incompatible wastewaters in common sewers.

Initially environmental regulations were developed, in many instances, through the mutual cooperation between steel plants, the regulatory authorities and engineering consultants retained by industry and/or the authorities. This process was necessitated because no one knew for sure what effluent standards could be met in a practical and economical way. Pilot tests had to be conducted and reasonable standards were set based on the ability of a treatment process to produce a specific effluent. Contaminants were limited to those that were obvious and readily detectable. They were, for the most part, suspended solids, oils, iron pH, etc. As new steel plants were planned and constructed, more sophisticated treatment schemes were required by the regulatory authorities who rightly felt that new, greenfield planning could produce treatment systems that would discharge wastewater that contained lower levels of contaminants and would achieve these levels economically.

This tightening of the regulations for new facilities had an impact, in addition, on the regulations imposed on existing facilities. Application of the new technology developed for greenfield sites to existing sites was a natural consequence. Some of the ideas that developed are as follows:

Hydrochloric Pickler Cascade Rinse System

In the pickling of steel, a rinse step is necessary to remove residual pickling acid and iron salts that adhere to the steel and cause staining and corrosion. Originally, rinse systems utilized several rinsing stages, each completely separated from the others. The rinse water from each stage was discharged directly to sewer. Resultant discharge rates for this type of rinse system vary from 700 to 1900 l/kkg (200 to 550 gal/ton) of steel pickled. Figure I is a schematic diagram of a typical rinse system of this type. All the rinse water from this type of system requires treatment prios to discharge.

A relatively recent development is the cascade rinse system where the steel leaving the pickler is rinsed with water which is then cascaded upstream towards the pickling tanks. The last rinse tank contains the freshest water. When spent, the rinse water is discharged, but because of the cascade configuration, only 50 to 200 l/kkg (14 to 55 gal/ton) of water is required which considerably reduces the amount of wastewater to be treated prior to discharge. Figure II is a schematic diagram of a typical pickler cascade rinse system.

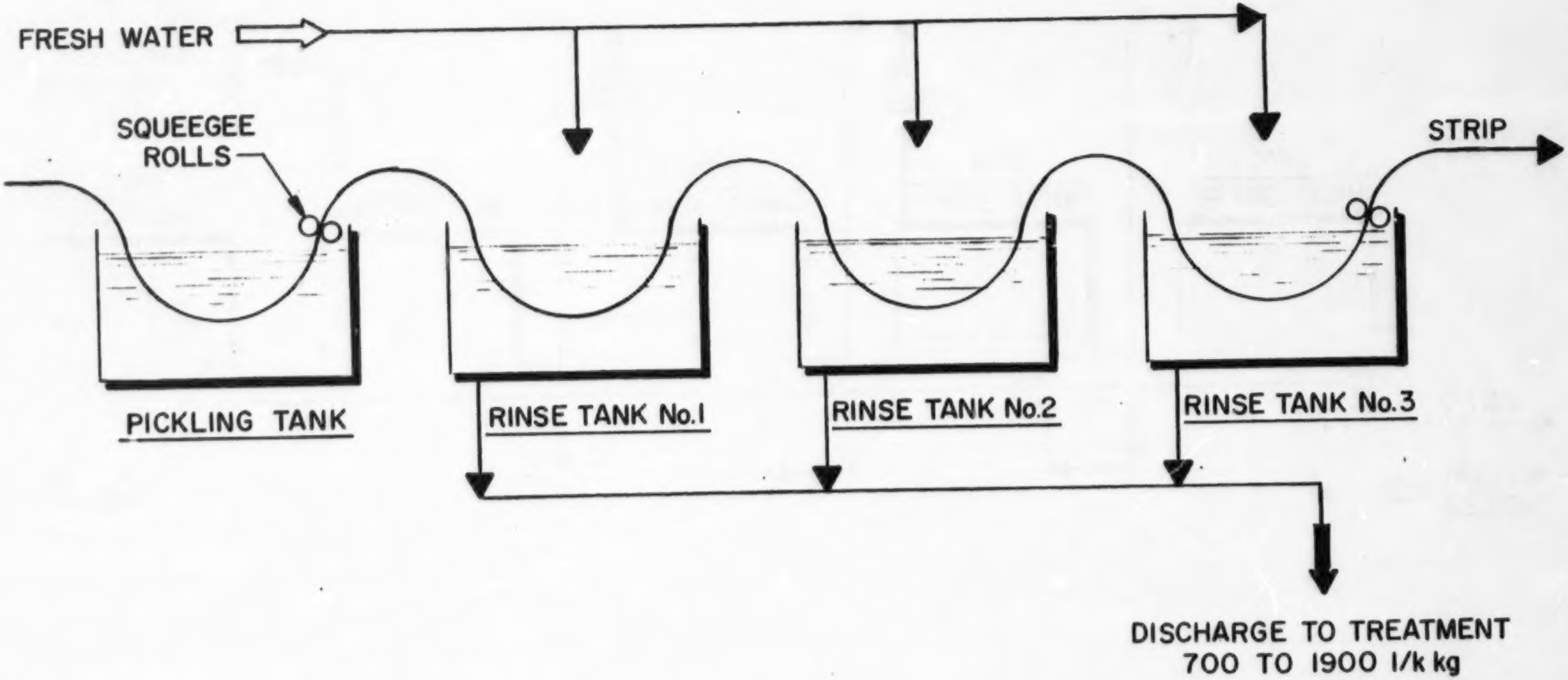

FIGURE I - TYPICAL PICKLER RINSE SYSTEM

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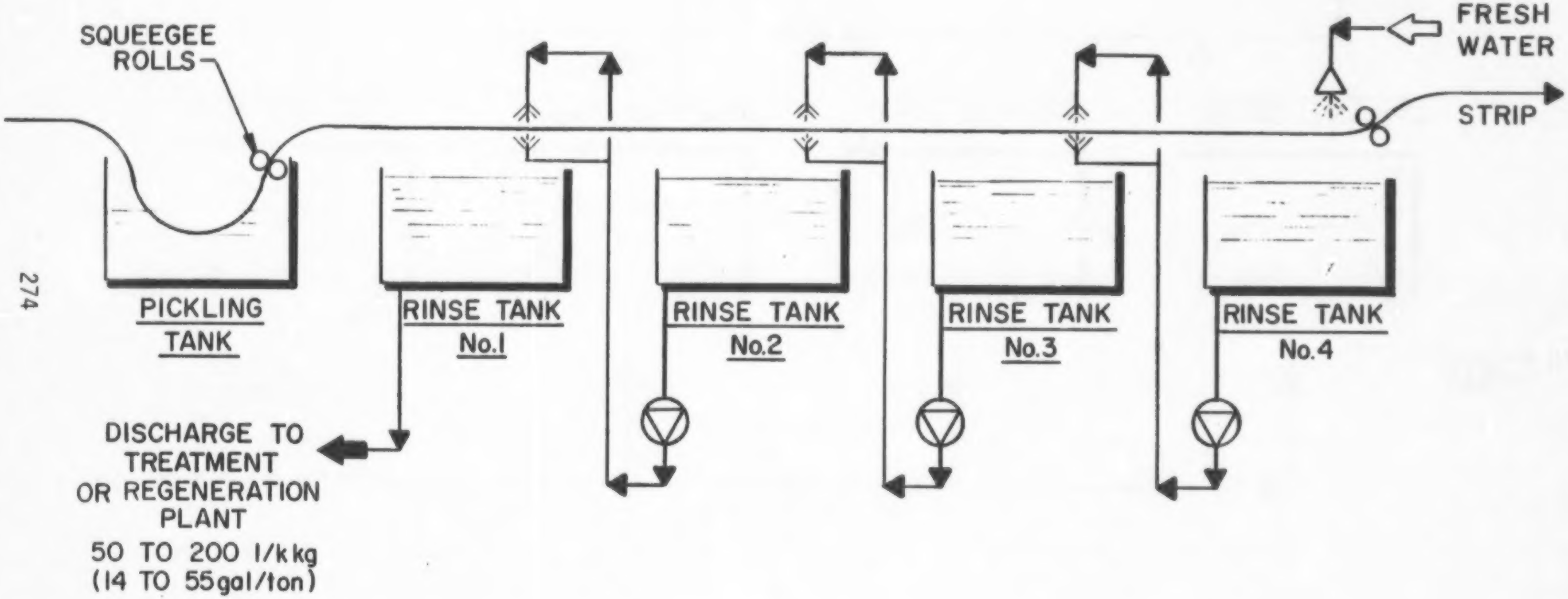

FIGURE II - TYPICAL PICKLER CASCADE RINSE SYSTEM

Cascade rinse systems can and have been retrofitted to existing pickler systems which, according to reports, are operating satisfactorily. It is obvious that the treatment facilities capital and operating costs will be significantly less for the reduced flow.

Elimination of Pickling Tank Heating Steam

Pickling baths must be maintained at elevated temperatures to permit proper pickling of steel. This elevated temperature is usually maintained by the injection of live steam into the pickling baths. This injection of steam has three results, namely: the bath is heated and maintained at the desired temperature, the steam causes vaporization of acid which must be cleaned with fume scrubbers, and the steam is condensed causing dilution of the pickling bath.

Temperature maintenance is the desirable aspect but vaporization and dilution are undesirable aspects of raw steam injection. If this injection can be eliminated then the two problems could also be eliminated or eased. Various means are available to heat the pickle acid baths such as submerged combustion, external heat exchangers and a furnace to heat the strip prior to its entrance into the pickling bath which would then bring the necessary heat into the tank to maintain the desired temperature. However, the furnace method requires a supplemental heat source for start-up conditions. These three methods are shown schematically on Figure III.

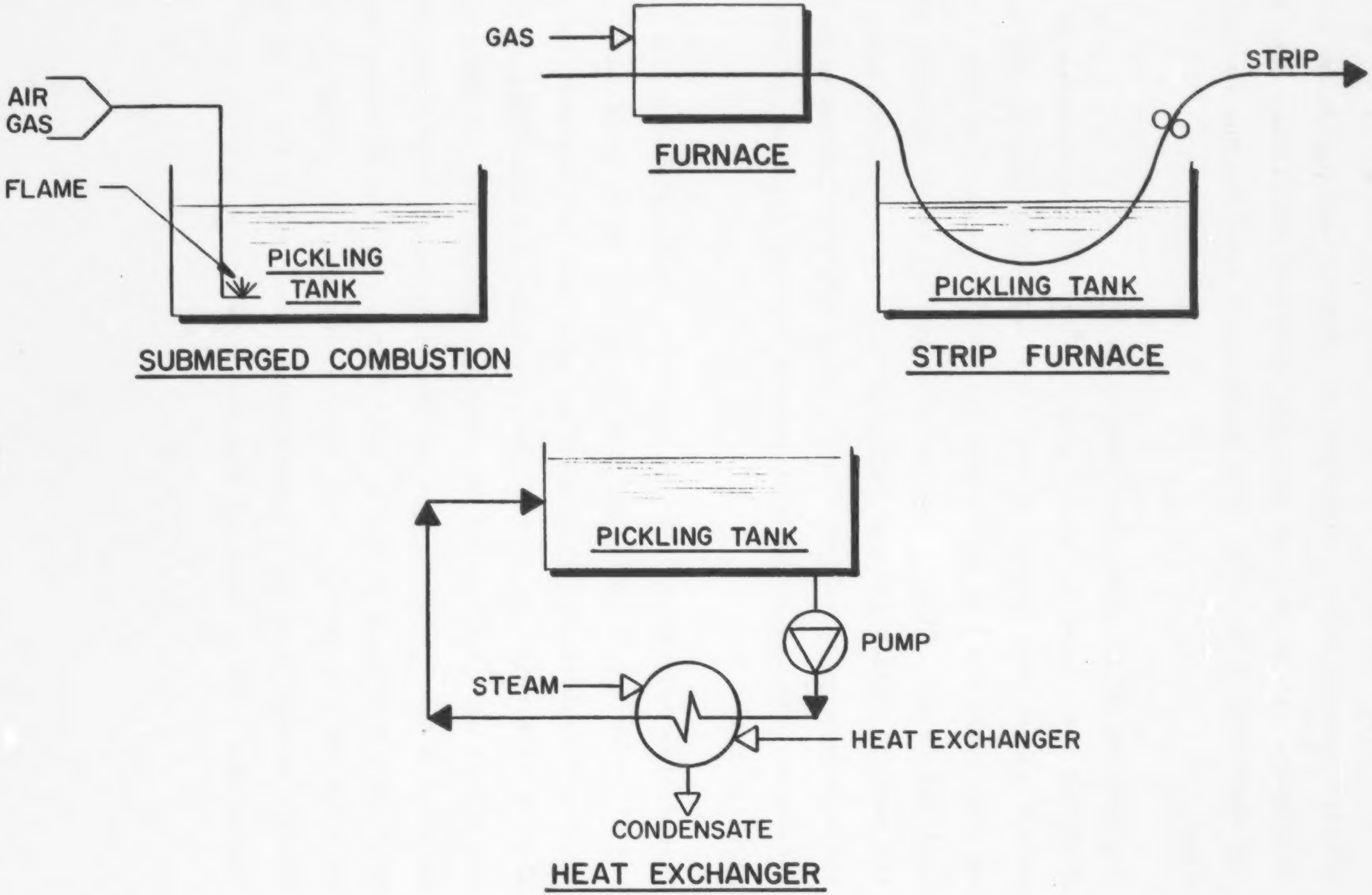

FIGURE III - ALTERNATE METHODS FOR MAINTAINING PICKLING TANK TEMPERATURE

Substitution of one of these methods can, for example, reduce the flow of waste pickle liquor from 14-18 m^3/hr (60-80 gpm) to 7 m^3/hr (30 gpm) for a pickler processing 1.5 x 10^6 mtpy. This 50% reduction would greatly reduce treatment and disposal costs or the costs to erect and operate an acid regeneration plant. Retrofit of any of these methods could be accomplished without problems during a period when a pickler is down for major maintenance.

Hot Mill Water Reuse and Conservation

Many methods are available to reduce the discharges of water from hot rolling mills. Any reduction in the amount of water discharged from this type of production facility will be significant since large amounts of water are required for cooling and cleaning purposes. Hot rolling facilities are usually composed of a reheat furnace, a forming section, a cooling section and, in the case of strip or skelp mills, a coiling section.

Large amounts of water are needed to protect various parts of reheat furnaces from the high temperatures encountered, but since this water is non-contact cooling water, it will not be discussed further except to add that the water uses for this application can be reduced and in many cases energy can be conserved by using the furnace cooling system as a steam boiler.

Coiler water is used for cooling, oil removal and for lubrication and becomes contaminated with oil, suspended solids and heat. It should be collected and treated with the wastewater that discharges from the mills' stands.

Large amounts of water are used to cool the steel strip on the runout tables of hot strip mills. The water is used to reduce the temperature of the steel strip from rolling temperature to coiling temperature in a relatively short period. To accomplish this, large amounts of water are applied. Although the temperature of the steel is reduced considerably, the water temperature does not increase very much due to the large volume necessary to achieve the rapid cooling effect desired. For instance, in cooling strip from 870°C (1600°F) to a coiling temperature of 565°C (1050°F), a change in steel temperature of 305°C (550°F), the temperature of the entire water system may increase only by approximately 10°C (18°F).

Cooling of this large amount of water is extremely expensive and, since contamination by suspended solids is minimal, elaborate treatment of the entire flow is not necessary. Usually the mill supplier recommends a blowdown from the runout table system to the mill stands section of between 20 and 30% of the water applied to the strip. This blowdown amount is to remove the heat and suspended solids contained in the water to prevent an unacceptable buildup. If, instead of blowing down this large amount of water, the runout table system water is treated in a segregated system there can be closer control of the water chemistry and, in turn, the amount of blowdown required may be reduced significantly.

This segregation will enable the operator to control the level of dissolved material, specifically chlorides, which affect strip staining. If a portion (20 to 30%) of the runout table water is filtered and cooled, the temperature will be maintained and the suspended solids levels will be acceptable for reuse. Chloride levels can be continuously monitored and a blowdown discharged to maintain the chloride level at an acceptable value. This is easily done in a greenfield installation and, surprisingly, in most existing mills it is not difficult to attain,particularly if the runout table system discharges to a sewer outside the mill building and can be intercepted easily.

Figure IV is a schematic diagram showing how these concepts have been applied at a greenfield hot strip mill.

General Concepts

At greenfield sites discussed in previous sections the concepts for maximum water conservation can, with little extra effort and cost, be designed into the plant water systems. However, at existing plants where production modifications cannot be made without considerable expense, wastewater treatment systems can be installed to optimize desired treatment to enable recirculation and also reduce pollution loads discharged.

Facilities Sizing

When a treatment facility must be installed to treat the wastewater from a production facility, the first stage is to establish the volume requiring treatment. The first source of information would be the most recent drawings showing water requirements and discharges. However, it may be dangerous to use these figures blindly because in many cases operators may have made modifications which were never added to "as-built" drawings. It is therefore necessary to undertake a field survey using the proper

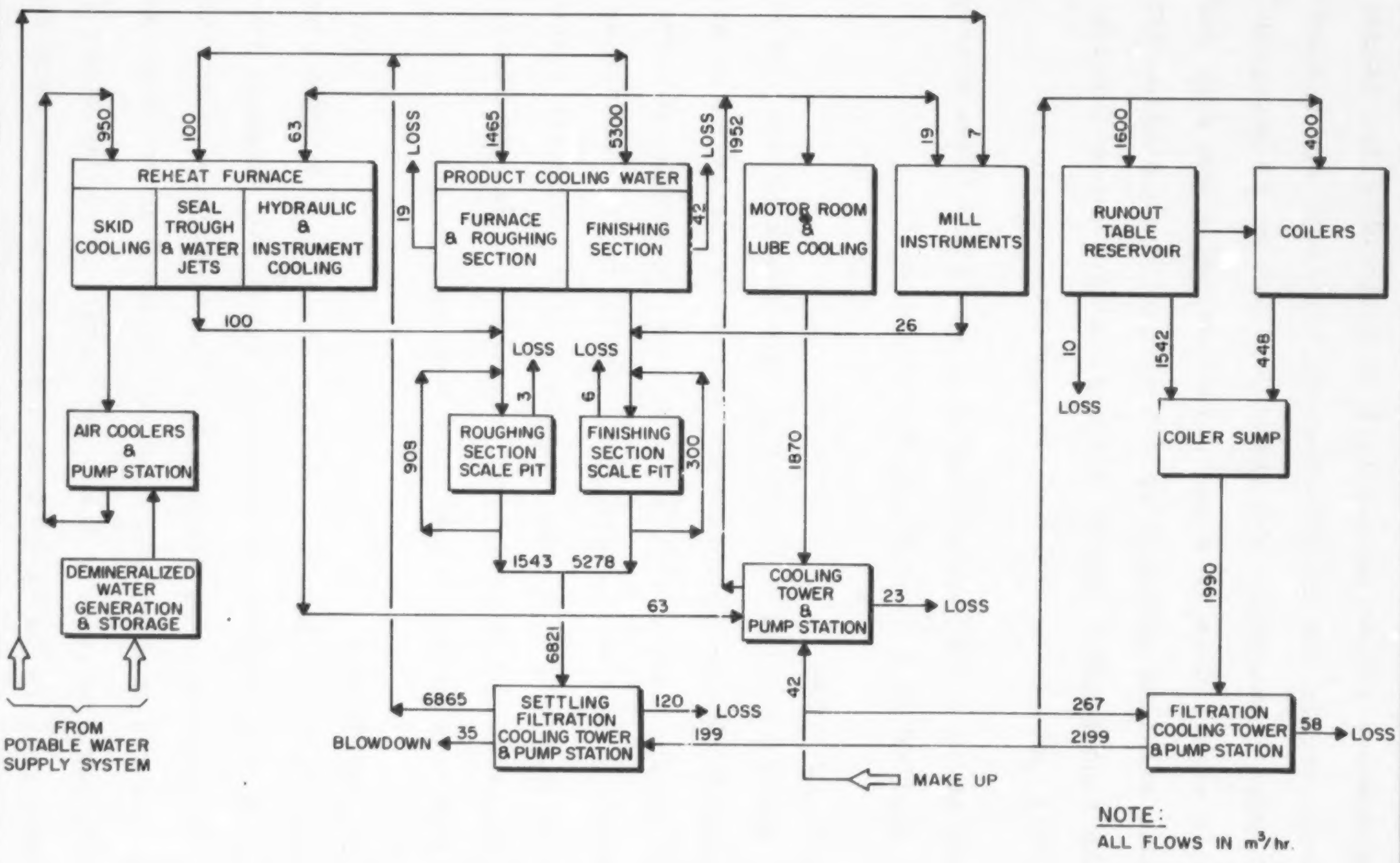
REHEAT FURNACE
SKID COOLING
SEAL TROUGH & WATER JETS
HYDRAULIC & INSTRUMENT COOLING
950
100
63
PRODUCT COOLING WATER
FURNACE & ROUGHING SECTION
FINISHING SECTION
1465
5300
19
LOSS
42
LOSS
1952
MOTOR ROOM & LUBE COOLING
MILL INSTRUMENTS
19
7
RUNOUT TABLE RESERVOIR
COILERS
1600
400
100
26
LOSS
LOSS
3
6
ROUGHING SECTION SCALE PIT
FINISHING SECTION SCALE PIT
908
300
1543
5278
6821
1870
10
LOSS
1542
448
COILER SUMP
1990
AIR COOLERS & PUMP STATION
DEMINERALIZED WATER GENERATION & STORAGE
FROM POTABLE WATER SUPPLY SYSTEM
63
COOLING TOWER & PUMP STATION
23
LOSS
42
MAKE UP
6865
SETTLING FILTRATION COOLING TOWER & PUMP STATION
120
LOSS
35
BLOWDOWN
199
267
2199
FILTRATION COOLING TOWER & PUMP STATION
58
LOSS
NOTE:
ALL FLOWS IN m³/hr.

FIGURE IV - HOT STRIP MILL WATER SYSTEM

techniques to determine what the actual flows being discharged are, and to establish the quality of the water so that the proper treatment unit operations, properly sized, can be installed. Not to perform the field survey may result in treatment facilities that are improperly sized. Oversized facilities are wastefut but the apparent economy of undersized facilities can also result in wasteful practices.

Sewer Segregation

Many of the older steel plants have common sewers which collect clean cooling waters, contaminated wastewaters and storm runoff. In the 1950s, most sanitary sewers had to be segregated from the other flows. The remaining combined sewers, in many cases, result in the necessity of installing treatment facilities that are hydraulically sized to treat not only the contaminated wastewater, but also clean cooling water. This is an extremely wasteful practice and serious consideration should be given to sewer segregation prior to construction of oversized treatment facilities. A properly performed survey can determine which flows may be eliminated from treatment requirements.

Although sewer segregation can be very costly, in the long run, the expenditure of monies to effect segragation can significantly reduce future operating costs.

Water Reuse

During the course of the recommended field survey, the qualities of water required for production operations would be identified. These qualities can be compared with allowable discharge qualities. A determination can then be made as to whether it is more economical to treat wastewaters for discharge, or for reuse within the facilities, or at some other production facility. Ideally, an entire plant should be treated as one water system so that treatment facilities can be optimized by combinations of compatible streams to be treated in one facility. Reusing water without treatment by cascading the blowdown from a high quality recirculating system as makeup to a system requiring lower quality wherever possible is the ideal. However, the quality will be degraded eventually to a point where treatment will be required. Geological constraints within individual plants usually preclude that sort of operation. It is therefore necessary that each plant be studied as an individual entity and each plant will be found to have its own optimum operating conditions.

THE REGENERATION OF NITRIC AND HYDROFLUORIC ACIDS FROM WASTE PICKLING LIQUID

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THE REGENERATION OF NITRIC AND HYDROFLUORIC ACIDS FROM WASTE PICKLING LIQUID

BY Hu Delu, Liang Xiuchung
and Wang Chingwen

INTRODUCTION

The scales formed on the surface of stainless steel during processing are usually removed by pickling with 7 - 15% nitric acid and 4 -8% hydrofluoric acid. This process has the advantages over other processes of high pickling rate, no overpickling and keeping the pickled steel with good appearance. The pickling liquid will lose pickling ability and become waste acid when its metal ion contents have reached a certain concentration through repeated pickling. The total acidity of waste acid is still rather high, which contains a large amount of iron, nickel and chromium salts. Nitric and hydrofluoric acids are strong corrosives, chromium is a strong toxicant, it should therefore be forbidden to discharge waste acid without being treated. Besides, nitric acid being expensive should be recovered and reused from the economic point of view.

Research work on treatment of waste liquid containing HNO_3 and HF has been carried out and some methods put into operation in the European countries, the U. S., Japan, etc. The chemical method can recover some useful matters, but it is complicated and needs a lot of equipment. It is a progress to use fluidized bed instead of fixed one in the ion exchange method, but it needs concentration of hydrochloric acid and treatment of dilute acid. The lower energy consumption and the availability of equipment and material are strong points of solvent extraction method, but further study is needed due to low recovery ratio of hydrofluoric acid. The vacuum evaporation method makes it possible to use material with high temperature and corrosion resistance, the acid recovery ratio is high as well. Up to now, it is the more effective recovery method.

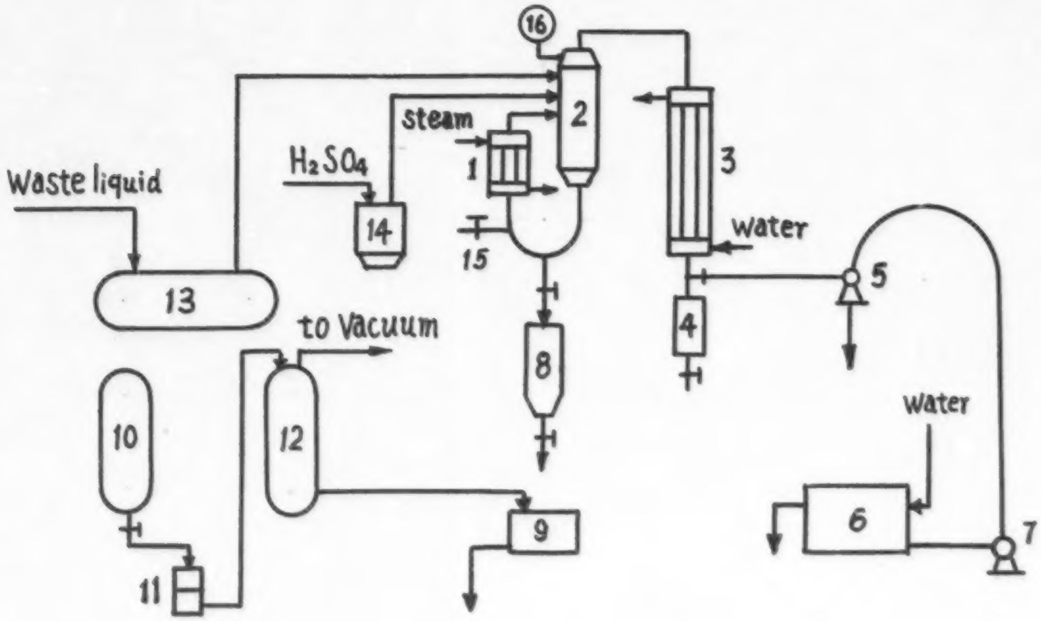
Based on the data obtained from pilot tests, a set of semi-continuous one-step HNO_3 and HF regenerating device by vacuum evaporation was designed for a seamless steel pipe shop in 1976 and put into operation in 1977. Its main feature is the use of corrosion resistant heater, evaporator and condenser. Later, an equipment for treating residual liquid after acids recovery was added and put into operation in 1979. Now, the waste liquid of the shop is no longer discharged and has been fully regenerated and reused. Moreover, nickel carbonate and ferrous sulfate can be recovered from the residual liquid. What is more, there will be no secondary pollution. Practice has proved that the vacuum evaporation method has the advantage of simple equipment, easy operation and high recovery ratio, it is therefore an effective recovery method.

ONE-STEP VACUUM EVAPORATION

Nitric and hydrofluoric acids are volatile, while sulfuric acid is not. The equilibrium temperature under atmospheric pressure of HNO_3, HF and H_2SO_4 are 87°C, 20°C and 300°C respectively. The mixture of nitric and hydrofluoric acids can be recovered based on their different partial vapor pressure. The method consists of adding sulfuric acid to waste acid, heating and evaporation. During evaporation, HNO_3 and HF are evaporated together with water, since H_2SO_4 has much lower partial vapor pressure than HNO_3 and HF. Nitrate and fluoric radicals displaced from metal salts by sulfate radical combine with hydrogen ion in sulfuric acid to form HNO_3 and HF, which are also evaporated, through condensation and recovery we obtain the regenerated acids.

The vacuum evaporation method is recommended to lower evaporation temperature, reduce corrosion and increase recovery ratio of HNO_3 and HF.

The vacuum evaporation method is of two kinds, i. e. one-step and two-step evaporation. Two-step evaporation comprises evaporation in two stages. The waste liquid is first evaporated in the 1st evaporation system for dehydration. The waste liquid concentrated, with H_2SO_4 added, is then reevaporated in the 2nd evaporation system, HNO_3 and HF are escaped to be condensed and recovered. It is suited to treat diluted waste acid obtained during pickling. One-step evaporation is a process used to recover mixture of HNO_3 and HF where the waste liquid flows continuously into the evaporation system without concentration and evaporates under vacuum. The equipment used in one-step evaporation is half of that in two-step evaporation. One-step evaporation is suited to treat undiluted waste liquid obtained during pickling. The process is shown below.



Flow sheet of regeneration of HNO_3 and HF from waste pickling liquid

1- heater, 2- evaporator, 3- condenser, 4- receiver, 5- injection pump, 6- circulating water pond, 7- water pump, 8- reactor, 9- centrifugal filter, 10- oxidizer, 11- filter, 12- precipitator, 13- waste acid metering control device, 14- H_2SO_4 metering control device, 15- air lift, 16- pressure guage.

Start injection pump, supply cooling water, suck certain volume of waste acid and concentrated H_2SO_4 into evaporator. Start air lift, heat with steam, add waste acid upon boiling, keep the liquid level in the evaporator unchanged, while HNO_3 and HF evaporate continuously and condense in the condenser, distilled liquid obtained is regenerated acid. Metal salts in waste liquid are continuously converted into sulfate, which remains in evaporator. When ferric ion concentration has reached the controlled value, stop evaporation, turn off heating steam, remove vacuum in regenerating system, transfer into reactor the residual liquid from evaporator, which is neutralized and reduced by iron filings. Nickel sulfide is precipitated by adding sodium polysulfide according to the nickel content and separated by centrifugal, the filtrate is used to produce ferrous sulfate. Clean nickel sulfide precipitate is oxidized and dissolved, from which iron is removed by adding sodium carbonate to form basic nickel carbonate.

OPERATING CONDITIONS OF VACUUM EVAPORATION PROCESS

Evaporation Conditions

The pressure of the heating steam is determined by the permeability and compression strength of impermeable graphite heater, it generally does not exceed 2 kg/cm^2 and is controlled at 1 kg/cm^2 during long-term operation.

Vacuum is a function of boiling point. The lower the vacuum, the higher the boiling point, and vice versa. Operating temperature is recommended not to exceed 65°C, since fibre-reinforced PVC plastics is used in evaporator and pipes. The vacuum should be 660 - 680 MM Hg.

To ensure complete evaporation of HNO_3 and HF, certain amount of

H_2SO_4 should be added, i. e. sulfuric acid needed to keep the concentration of circulating H_2SO_4 at 12.5 N plus sulfuric acid needed to transform nitrate and fluorate into sulfate.

Acid recovery ratio will decrease if concentration of circulating H_2SO_4 is too low. If it is too high, iron salts will crystallize ahead of time and amount of waste acid to be treated is reduced.

It is determined by pilot tests that in the process sulfuric acid should be discharged as residual liquid when ferric ion concentration in the circulating H_2SO_4 has reached 75 g/l, otherwise crystallization will take place and the heater will be blocked up. Impermeable graphite impregnated with fluorine containing polymer has been developed to make heat exchanger, the key equipment for recovering HNO_3 and HF. A series of tests show that impermeable graphite is chemically stable and has excellent heat conductivity, impermeability, strong oxidation resistance and non-fouling property. It has been successfully used in several plants since 1974. The development of this kind of material has opened up a new path for the development of corrosion resistant heat conducting material.

Treatment of Residual Liquid

Sulfuric acid in discharged residual liquid is neutralized in the reactor by iron filings, while ferric ion is reduced to ferrous ion. Iron filings react intensely with 20% H_2SO_4, therefore, in order to shorten the reaction time, the residual liquid after discharging into the reactor should be diluted with water, then neutralized by adding iron filings. In this way, pH of the solution can quickly increase to 2 - 3.

Nickel salt reacts with sodium polysulfide at pH 2 - 3 to form nickel sulfide precipitate. Through filtration, the precipitate is separated from ferrous sulfate solution. The precipitate can be oxidized and dissolved by dilute HNO_3.

The ferrous ion inclusions in nickel sulfide is oxidized into ferric ion, which forms $Na_2Fe_6(SO_4)_4(OH)_{12}$ precipitate with sodium carbonate added, precipitate is removed by filtration, pure nickel nitrate solution is obtained, when its pH is about 3. At the end of reaction pH is controlled up to 4. Clean nickel nitrate solution reacts with sodium carbonate solution under heating to form basic nickel carbonate precipitate, which can be used as raw material for nickel electrolysis after filtration, washing and drying.

OPERATION PRACTICE

Measurement has been made for waste acid recovery project of a steel plant after 3 years operation, recovery data are shown below.

Items	Volume (l)	Content					
		H^+(N)	F^-(N)	NO_3^-(N)	Fe^{+++}(g/l)	Ni^{++}(g/l)	Cr^{+++}(g/l)
waste acid	1140	2.58	2.67	1.70	21.50	3.58	4.27
residual liquid	350	13.47	0.88	0.23	80.05	12.30	13.7
regenerated acid	858		3.29	2.12			
sulfuric acid	150	32.4					
recovery ratio (%)			92.9	93.9			

The recovery ratio of nickel is 85%. From the calculation based on the composition of waste acid, 8 kg of basic nickel carbonate can be recovered per M^3 of waste acid.

The recovery of waste acid not only controls environmental pollution, but also leads to significant economic results. Regenerating 1 M^3 of HNO_3 and HF mixture results in a saving of 478.1 yuan. Details are shown below.

Items	recovery		consumption				
	98% HNO_3	42% HF	electricity	water	steam	H_2SO_4	wages
Quantity	117 kg	134 kg	50 KWH	300M^3	2 T	270 kg	3.3 people
Value (yuan)	58.5	509.2	4.2	10.8	14.0	54.0	6.6 .
Total (yuan)	567.7		89.6				

The capacity of the regenerating device put into operation in the steel plant is 1 M^3 of regenerated acid per shift. The capital cost of the device is 130,000 yuan, which can be paid off in one year.

CONCLUSION

1. To recover HNO_3 and HF by one-step vacuum evaporation has the advantages of simple equipment, easy operation, high recovery ratio and significant economic result.
2. The process has solved environmental protection with no secondary pollution.
3. The residual liquid can be treated to recover nickel carbonate and ferrous sulfate.

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STEEL INDUSTRY PICKLING WASTE AND ITS IMPACT ON ENVIRONMENT

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ABSTRACT

This study was directed to develop information on ferrous sulfate heptahydrate (copperas) produced by the steel industry. Several major aspects of copperas generation and disposal were studied, and these are:

1. Pickling waste generation in integrated steel industry and by secondary processors, present practice, and future directions.
2. Waste pickle liquor disposal technology and future development.
3. West European pickling technology, centralized zonal waste pickling liquor treatment concept and co-treatment of different industrial waste streams.
4. Ferrous sulfate heptahydrate production and end-use.

The study shows that out of 60 million tonnes pickled, about one-third is pickled with sulfuric acid, but except for very small amounts going to the pigment industry, most of the waste is disposed of without any recovery of either free acid or dissolved iron units. Most of the 75,000 tonnes/year of iron sulfate crystals produced are from secondary industries while commercial plants produce a similar quantity for pigment production starting from scrap and sulfuric acid. While pigment production is more than one-half of the present market for copperas, potentially the largest future market for copperas is likely to be sewage treatment plants.

The study also shows that the rapid changeover from H_2SO_4 to HCl pickling has ended and the relative price structure between the two acids may favor H_2SO_4 in the future. However, all green-field plants are likely to use HCl pickling because the end product, if recycling is practiced, is Fe_2O_3 which can be utilized in the plant itself.

Satisfactory copperas production technology exists, and market expansion into water-sewage treatments may require a rapid expansion of copperas production units --particularly, if regional centralized facilities are encouraged and established on a cooperative basis, each member paying for its service proportional to the volume of acid waste treated and getting commensurate credit for acid recovered.

Several recommendations have been made for additional research and regulatory modifications to aid and enhance greater use of copperas.

INTRODUCTION

An estimated 60 million tonnes of steel products are pickled every year in the U.S.A. resulting in a pickle liquor volume of about one billion gallons per year. Of this volume, over 85% are generated by 18 large steel corporations and the remaining 15% at the several hundred smaller plants and batch processing units located all over the country. Recycling of waste pickle liquor and its disposal without harming the environment are causes of major concern to both the industry and EPA. This study was performed to develop information to minimize the impact of steel industry ferrous sulfate heptahydrate waste on environment. Additional information on hydrochloric acid pickling technology and its bearing on sulfuric acid pickling has been considered where necessary. The pickling practice and waste pickle liquor disposal in foreign steel plants has also been reviewed. Selected references are cited and recommendations made for additional research and development.

THE MAGNITUDE OF PICKLING WASTE

Pickling in the U.S. Steel Industry

The bulk of pickling waste is generated by integrated steel plants located at 61 sites.[1] In addition, 35 specialty steel companies (48 locations), and 37 scrap/sponge iron-based steel plants (55 locations), are widely distributed in the U.S.[2] A far larger number (689) of small manufacturers and fabricators of steel mill products are distributed over the country.[3] These smaller companies operate primarily via batch processes. The total tonnage treated by them may be as large as 10 to 15% of total national steel shipment.

Growth in raw steel production and steel shipment has shown significant fluctuations during the last 20 years. Annual steel production and shipment data for 1956 to 1978 are given in Table 1.[4,5] Various projections have been made regarding steel consumption and raw steel production by 1985 and beyond, based on long-term trends.[6,7] Based on 2% growth rate, the projection indicates a raw steel production of about 153 × 10^6 tonnes by 1985. To produce 153 × 10^6 tonnes by 1985, the installed capacity must increase by about 25 × 10^6 tonnes. This additional capacity can be obtained by expansion of present facilities and/or by constructing new green-field plants. In green-field plants, the chances are that the most technologically advanced pickling systems will be installed, very likely based on HCl with regeneration. This will not affect the present ferrous sulfate pickle liquor disposal problem. If, however, a large fraction of the 25 × 10^6 tonnes additional capacity is added by expansion of existing units (primarily because of capital shortage), then some or all of the sulfuric acid pickling units already in use are likely to be retained and extended, thereby significantly aggravating current waste sulfuric acid pickle liquor disposal problems.

Table 1 shows that the ratio of steel pickled to steel shipment ranged from 0.54 to 0.66 with a long-term average of 0.63. Unless the product mix changes significantly during the next few years (due to material substitution in automobile, container, and other industries), a ratio of 0.63 may be expected to be maintained until 1985. Thus with 112 × 10^6 tonnes of steel shipment by 1985, about 71 × 10^6 tonnes of steel will require pickling.

The steel pickling process generates wastes from three distinct sources: (a) waste pickle liquor from acid baths, (b) acidulated rinse water from washing acid drag-out from the pickling baths, and (c) acidified water generated in cleaning acid vapors and mists from the pickling baths. The waste pickle liquor is relatively small in volume when compared with the other two waste streams. In H_2SO_4 pickling (with 1% iron loss), a typical pickle liquor contains 8% free acid and 8% dissolved iron and is generated at a rate of 105 l/tonne of steel; with HCl, the corresponding figures are 1/2 to 1% free acid, 10% dissolved iron, and 50 l/tonne.

Rinse waters pose a different kind of problem because of the large quantities needed. Some large continuous strip mills may use as much as 3.8 m^3/min, but most mills use about 1.5 m^3/min. Batch-type pickling plants use less water than the continuous plants, i.e., 0.1 to 1.1 m^3/min. Fume scrubbing water is usually combined with rinse water for treatment.

Present Disposal Techniques for Waste Pickle Liquor (WPL)

At present, the 3.8 × 10^6 m^3 of waste pickle liquor is handled in many different ways, but the least common method is recycling and recovery of acid and the lost iron values. A loss of 1% iron value may amount to 700,000 tonnes by 1985—almost one-third billion dollars! Similarly, the loss of free acid thrown away amounts to many million dollars.

Waste pickle liquor (WPL) is disposed by:

1 Contract hauling.
2 Deep well injection.
3 Neutralization/oxidation and lagooning.
4 Dumping in ocean/lake/river/alkaline beds.
5 Co-treatment with municipal waste.

Contract Hauling. Contract hauling avoids the immediate problem but appears to be a relatively expensive means of disposal, i.e., \$36/m^3.[8] Several large steel plants and many batch processors use contract hauling. Industrial waste disposal by contract hauling is an established industry and may become a more significant industry in the near future.[9] However, additional studies are needed in co-treatment of different wastes to recover valuable metallics and reduce expenses. Or, the waste may be heated and converted to a form acceptable for sewage conditioning in a municipal waste system. The complexity of treatment needed dictates the total cost of hauling. For example, a simple treatment may be as low as \$26/m^3, a more complex processing \$48/m^3, and difficult wastes, such as mixed chlorinated hydrocarbons, as high as \$79/m^3.[9] (All these costs are based on ref. 9, escalated to reflect the 1970-1978 price trend.)

Deep Well Injection. There are several hundred injection wells in the U.S.,[10,11] some accept pickle liquor at the rate of as much as 5 m^3/min and are as deep as 3660 meters. Only a few of them are used for disposal of waste pickling liquor. Before disposal, the pickle liquor requires careful filtration because otherwise the well pores clog, blocking infiltration. Several large steel plants use deep wells for disposal of waste pickle liquor. Operating costs vary up to \$2.60/m^3.[12] This is much less expensive than contract hauling. However, this disposal method is being phased out.

Neutralization/Oxidation and Lagooning. Neutralization of the highly acidic WPL with lime, soda ash, or caustic soda was practiced for a long time. The treatment increased the pH to neutral, and iron precipitates as a gelatinuous iron hydroxide sludge which may not settle in 20 years! Usually, large lagoons were created, e.g., WPL from one million tonnes of steel on neutralization results in about 200,000 tonnes of sludge requiring a lagoon one meter deep spread over an area 200 m by 1 km. The cost for simple neutralization may range up to \$13/m^3.[12] In addition to the simple cost of neutralization and lagooning, the cost of total energy requirement in the form of lime production must be considered. It requires about 2.78 million kcal to produce 1 tonne of quicklime (CaO), and the cost of lime, which went from \$20/tonne in 1972 to \$35/tonne in 1976,[8] may increase significantly by 1985

This simple lime neutralization/lagooning process can, however, be modified to incorporate vacuum filtration and disposal of a wet cake, 62% water, as practiced by H. H. Robertson Co., Ambridge, Pennsylvania.[13] This waste disposal technique minimizes space requirements (at the expense of additional capital and operating costs), but neither energy saving nor recovery of any metallic or other product values is obtained.

A DuPont process[12] uses controlled neutralization and oxidation with air to yield a mixture of magnetite (Fe_3O_4) and $CaSO_4$, which can be easily dewatered. The $CaSO_4$ may find a market as wallboard raw material. Bethlehem steel plant at Burns Harbor, Indiana, originally used the DuPont neutralization processes to treat H_2SO_4 WPL.

Table 1

STATISTICAL DATA, UNITED STATES INDUSTRY[4,5]

Year	Raw Steel, 10^6 tonnes[a]	Steel Shipment, 10^6 tonnes[a]	Steel Shipment/ Raw Steel	Steel Pickled, (Estimates) 10^6 tonnes[a]	Steel Pickled/ Steel Shipment
1956	104.5	75.6	0.72	45	0.59
1957	102.3	72.5	0.71	39	0.54
1958	77.4	54.4	0.70	35	0.65
1959	84.8	63.0	0.74	41	0.64
1960	90.1	64.6	0.72	43	0.66
1961	88.9	60.0	0.67	39	0.65
1962	89.2	64.1	0.72	42	0.66
1963	99.2	68.6	0.69	45	0.65
1964	115.3	77.0	0.67	49	0.63
1965	119.2	84.2	0.70	53	0.62
1966	121.7	81.7	0.67	50	0.61
1967	115.4	76.1	0.66	47	0.62
1968	119.3	83.4	0.70	53	0.64
1969	128.2	85.2	0.66	54	0.63
1970	119.3	82.4	0.69	51	0.62
1971	109.2	78.9	0.72	51	0.64
1972	120.9	83.3	0.69	55	0.66
1973	136.8	101.1	0.74	67	0.66
1974	132.2	99.4	0.75	62	0.63
1975	105.8	72.6	0.69	43	0.60
1976	116.2	81.1	0.70	(51)[b]	(0.63)
1977	113.7	82.7	0.73	(52)	(0.63)
1978	124.0	87.1	0.70	(55)	(0.63)
1985	153	112	0.73	(71)	(0.63)
Projected					

[a] 1 tonne = 1000 kg = 1.102 ton
1 ton = 2000 lb

[b] Figures in parentheses are estimates based on 63% of all shipment being pickled.

Interlake Steel uses an Interlake-DuPont modification process at its plant in Chicago, Illinois, which produces magnetite and calcium chloride from HCl WPL. The $CaCl_2$ solution is treated with H_2SO_4 to regenerate HCl[12] and to precipitate $CaSO_4$ which may be utilized. In both the DuPont and modified neutralization processes, iron values are recovered. The Fe_3O_4, can be pelletized and used as a blast furnace feed, or it can be converted and used in ferrites, magnetic tape, pigment, and other industries.[14,15]

Dumping in Ocean/Lake/River/Alkaline Beds. 'If WPL is diluted sufficiently, then it can be tolerated' is the principle governing dumping in large bodies of water such as ocean and river. Bethlehem's Lackawanna and Sparrow's Point plants had permits to discharge WPL in Lake Erie, New York, and Patapsco River, Maryland, respectively. Many states and local authorities had given permits to steel plants in the past. With more stringent regulations, the steel industry is actively examining alternatives to dumping in public rivers and lakes.

All steel plants have large slag dumps, and the WPL can be dumped on them. The alkaline slag neutralizes a part of the free acid, but the dissolved iron is not converted to a stable form. Runout from these dumps would contain appreciable concentration of iron salts and have to be treated by the storm water drainage system, which usually discharges either to a river/lake/ocean or to the local municipal system. If hot slag is quenched, acid pollutants are transferred to the air and there is more widespread cause for concern.

Treatment of Municipal Waste Water. Tertiary water treatment of municipal waste water for removal of phosphates is opening up new markets for iron and aluminum salts. From 10 plants in 1968, the number of tertiary treatment plants increased to 445 in 1972[16] and may have increased significantly since then. The common chemicals that can be used to react with phosphates and to remove them as salts are ferric and ferrous chloride, ferric and ferrous sulfate, aluminum sulfate (alum), sodium aluminate, lime, and WPL ($FeCl_2$ and $FeSO_4$). Currently lime, ferric chloride, and alum are the main chemicals used. Lime has run into worker opposition at sewage plants. It is also a highly energy-intensive product. Between Al and Fe salts, iron appears to be preferred.

A report by KSF Chemical Processes, Ltd., Cambridge, Ontario, Canada[5] shows that about 1 tonne of heptahydrate is required to treat 3800 m^3 of sewage.

Sewage treatment plants around the Great Lakes area alone treat approximately 76 million m^3/day and may require as much as 20,000 tonnes of heptahydrate per day. The steel plants in this area, if all plants use sulfuric acids, can only produce about 2000–4000 tonnes of heptahydrate per day and will be inadequate to fill the demand.

ACID REGENERATION AND/OR IRON RECOVERY-- STATE OF ART, U.S.A. AND FOREIGN

Hydrochloric versus Sulfuric Acid Pickling

In an EPA Technology Transfer Capsule Report,[8] the economics of the different competitive processes have been carefully analyzed for sulfuric acid pickle wastes. On the basis of certain assumptions, it was estimated that for plants with pickling capacity of 45,000 tonnes/yr or more, H_2SO_4 recovery is economical even when no credit is given for the heptahydrate crystals.

Information is, however, quite fragmentary in the open literature regarding the steel industry pickling capacities in terms of H_2SO_4 vs. HCl units with regeneration, and the type of regeneration practiced. Private estimates[5] indicate that the number of HCl lines (about 60) exceeds that of H_2SO_4 lines (about 30). On the other hand, HCl acid consumption is less than H_2SO_4 acid use. This is so because about 19 kg H_2SO_4 (100%) is required to pickle one tonne of steel resulting in about 105 liters of WPL. The corresponding quantities for HCl are about 6.5 kg of 100% acid/tonne of steel resulting in about 50 liters of WPL. It has been estimated[5] that out of about 60 million tonnes of steel pickled in 1974, about two-thirds were pickled by HCl and one-third by H_2SO_4. HCl and H_2SO_4 acid costs increased during 1966 to 1976 from $48 to $67/tonne and $10 to $32/tonne, respectively.[17] The rapid conversion from H_2SO_4 to HCl pickling which occurred during the 1960's has stopped, and a relatively cheaper H_2SO_4 may make it more attractive for pickling. SO_2 emission control regulations may generate a large surplus of S in the 1980's.[18]

Hydrochloric Acid Regeneration Processes, U.S.A. and Canada

HCl regeneration is known to be practiced in only eight plants in the U.S.A. and Canada.[11] Spray roasting, known as the Woodall-Duckham-Ruthner process, and fluidized bed roasting, known as Keramchemie-Lurgi, are well established in the U.S.A. and foreign countries, and are described fully in the literature. The resulting products are regenerated HCl and granular iron oxide, which is usually used as a sinter feed for blast furnace.

The sliding/vibrating roaster process, the ETI Process[11] (Environmental Technology, Inc.), uses a unique roaster reactor design combining a spray roaster principle with a vibrating moving grate for iron oxide removal. The oxide particle size is larger than that produced by both spray and fluidized roasting processes, and the dust removal problem is minimized.

The low-temperature PORI[19] chemical process is completely different from the high-temperature processes. It consists of four major operational stations: evaporator, oxidizer, hydrolyzer, and a falling film condenser-absorber system. At the evaporator, the $FeCl_2$ concentration is raised from a typical 20% to 36%. In the oxidizer, $FeCl_2$ is oxidized to $FeCl_3$ and Fe_2O_3 followed by $FeCl_3$ hydrolysis to HCl and more Fe_2O_3. The Fe_2O_3 is dense and can be recycled to steel production. The HCl produced is 30% concentrated with 99% yield and is recycled to the process.

Sulfuric Acid Regeneration Processes, U.S.A. and Canada

All the regeneration systems recover the free acid by removing the iron salts from the WPL. There are 32 plants in operation in the U.S.A. and Canada, as shown in Tables 2 and 3. The two basic processes are (1) heating type, producing $FeSO_4$ monohydrate (5 plants), and (2) cooling type, producing $FeSO_4$ heptahydrate (27 plants).

In the continuous Sulfex process,[11] a submerged zirconium heat exchanger heats WPL to 125 C with 690 KPa steam; the acid concentration reaches 45% to 50%, and $FeSO_4 \cdot H_2O$ precipitates out. After crystal separation, the recovered acid containing about ½% Fe is returned for pickling.

The continuous Pureco process[11] uses submerged combustion heaters to heat WPL to 95 C and concentrate the acid to 35%. The iron precipitates out as $FeSO_4 \cdot H_2O$, and the recovered acid containing ½% Fe is recycled.

In the cooling type continuous Keramchemie process,[11,20] the WPL is precooled and then flows to a crystallizer where the temperature is decreased to 5 C using high-pressure steam ejectors. The acid/crystal slurry is concentrated and centrifuged. The recovered acid containing 2-3% Fe is recycled. The large flow of ejector condensing water is slightly contaminated with entrained WPL.

In the batch type Crown Chemical process,[3] the WPL is chilled through a Freon refrigeration system to about 0 C in about 8 hr. The heptahydrate is concentrated in settling tanks and filters.

The 24 KSF Process units[11] are modular batch type. The WPL is cooled with chilled recirculating water circuit. The solution is cooled to 7 to 10 C, the heptahydrate crystals are discharged by gravity, washed, partially dried, and discharged. The recovered acid is reheated and recycled at a concentration of 25% containing 2 to 3% Fe. The process is "zero discharge" incorporating full recycling of all acid mists, spent acid, and pickling rinse waters.

The planning for additional pickling units in steel plants is not readily available in the open literature. Private information indicates that Bethlehem (Sparros Point, Maryland), Jones and Laughlin (Aliquippa, Pennsylvania) and U.S. Steel (Fairfield, Alabama) may use H_2SO_4 pickling more significantly during the next five years. Other steel plants, such as Armco (Ashland, Kentucky), National (Weirton, West Virginia), Jones and Laughlin (Cleveland, Ohio), and Republic (Gadsden, Alabama) may significantly enlarge HCl pickling practice with regeneration. It is expected that during 1980-85 the addition of 25×10^6 tonnes steel capacity will require establishment of at least one (U.S. Steel-Conneaut), and perhaps two greenfield plants in addition to the above and several more unannounced rounding-off facilities requiring pickling plant additions.

European Steel Plants

Western Europe raw steel production was 154 million tonnes in 1977. On an equivalent tonnage basis, WPL production in European steel plants is slightly less because of the difference in product mix. In the U.S.A., the proportion of flat products in the product mix is relatively more than in Europe, and WPL generation is maximum in flat product pickling. In addition to the integrated steel plants, European secondary and tertiary fabricators and processors use similar batch pickling processes and have similar problems, if not more so because of less disposal elasticity in land surface and water bodies. On the other

Table 2

TYPES OF SULFURIC ACID REGENERATION PLANTS AND THEIR LOCATIONS IN THE U.S.A. AND CANADA[11]

Type	Plants
By Heating (monohydrate)	
Sulfex Process (Sulfex Corporation, Maple Heights, Ohio)	Metal Processing Co. Maple Heights, Ohio
Pureco Process (Pureco Systems, Inc. Mt. Prospect, Ill.)	Joselyn Manufacturing & Supply Co. Chicago, Ill.
	Empire Galvanizing Div. of Joslyn Steel Chicago, Ill.
	H. H. Howard Company Chicago, Ill.
	Budd Company Frankfort, Ohio
By Cooling (heptahydrate)	
A. Vacuum Type	
Keramchemie Process	Fitzsimons Steel Company Youngstown, Ohio
	Sivaco-Ingersoll, Ltd. Ingersoll, Ontario, Canada
	Sidbec-Dosco, Ltd. Rexdale, Ontario, Canada
B. Refrigeration Type	
Crown Process (Crown Chemical Co., Inc., Indianapolis, Ind.)	Laclede Steel Company Alton, Ill.
KSF Process (KSF Chemical Processes, Ltd., Cambridge, Ontario, Canada)	24 Plants (See Table 3 for locations)

Table 3

LIST OF KSF PICKLING AND ACID RECOVERY SYSTEMS[11]

Wimco Steel Sales, Ltd.
1430 Martingrove Road
Rexdale, Ontario

P. L. Robertson Manufacturing Co., Ltd.
Bronte Street
Milton, Ontario

Atlantic Wire Company
One Church Street
Branford, Connecticut

Motor Wheel Industries
(Chatham) Ltd.
650 Riverview Drive
Chatham, Ontario

Macwhyte Company
2906 14th Avenue
Kenosha, Wisconsin

Electric Wheel Company
1120 North 28th Street
Quincy, Illinois

Firestone Street Products of Canada Ltd.
31 Firestone Blvd.
London, Ontario

National Fence Company
Bladensburg, Maryland

Russell, Burdsall &
Ward Company
Rock Falls, Ill.

Nelsen Steel & Wire Co.
9400 West Belmont
Franklin Park, Ill.

Thompson Steel Co., Inc.
9470 King Street
Franklin Park, Ill.

Republic Wire Corp.
500 Blair Road
Carteret, New Jersey

Everlock Division
(Microdot Inc.)
Detroit, Michigan

Metal Products Division
Goodyear Tire & Rubber Co.
1144 East Market Street
Akron, Ohio

Motor Wheel Corporation
1600 North Larch Street
Lansing, Michigan

Motor Wheel Corporation
Ogletown Road
Newark, Delaware

Igoe Brothers, Inc.
234 Poinier Street
Newark, New Jersey

Walker Wire & Steel Co.
660 East 10 Mile Road
Ferndale, Michigan

New York Wire Mills Corp.
3937 River Road
Tonawanda, New York

Bethlehem Steel Corp.
Lackawanna, New York

American Chain & Cable
Co., Inc.
American Chain Div.
(Office)
East Princess Street
York, Pennsylvania

Atlantic Steel Company
16th & Holly Streets
Atlanta, Georgia

Krueger & Company, Inc.
900 Industrial Drive
Elmhurst, Ill.

Sivaco Wire & Nail Co.
800 Quellette Street
Marieville, Quebec

Boric Kidric Steelworks
Niksic
Yugoslavia

hand, the close proximity of many secondary plants allows development of central treatment facilities with economy-in-size benefits which their counterparts in the U.S.A. may not enjoy. At Altena in West Germany, an HCl acid recovery plant is owned and operated jointly by 30 smaller companies drawing wire and/or galvanizing. Tankers collect spent liquors and return recovered acid to the works. The oxides recovered are sent to the steelmakers. The companies so served by this central recovery plant are situated within an 80 km (50 mile) radius.[21]

A summary of the pickling processes practiced in the different European plants is given in Table 4. Two steel plants have only sulfuric acid pickling, four have only hydrochloric acid, and two have both. One plant is changing over from H_2SO_4 to HCl, and another is planning to change.

Three sulfuric acid pickling lines recover heptahydrate and use it for water treatment, in the sintering plant for conversion to oxide, as animal feed additive, and also for discharge on a slag dump.

Of the six plants using HCl pickling, five regenerate the acid and produce Fe_2O_3 as a by-product. Heating for regeneration is done using either oil, natural gas, or coke oven gas. Four of the five regeneration units use the spray roasting technique and obtain a very fine reddish-brown Fe_2O_3. One unit uses a fluidized bed roaster and generates a much coarser gray iron oxide product.

Most of the Fe_2O_3 is used either in the ferrite industry or at the sinter-pelletizing plant. There seems to be no significant problem in Fe_2O_3 disposal.

The steel plants consider HCl pickling to be a better process than H_2SO_4 pickling. It is faster, gives a better looking pickled surface, and the acid can be regenerated (99%) with a by-product which is eminently salable and usable. The process requires energy, and if oil and natural gas have to be used instead of the coke oven gas within the steel plants, then it will also be more expensive in the near future. The process also has some maintenance problems.

If the H_2SO_4 pickling line has a substantial scale breaker, then H_2SO_4 pickling may become equally as fast as HCl pickling, as opined by one steel pickler. While HCl directly dissolves FeO (scale), H_2SO_4 operates better if it can readily get below the scale and attack the metal surface and there lies the significance of scale breaking before pickling.

HCl pickling gives a brighter sheet. However, if the pickled products are to be eventually cold rolled (as most are) the initial relative brightness of HCl pickled sheet has no special advantage over H_2SO_4 pickled sheets before cold rolling because of their brightness alone.

On the other hand, it was noted that $FeSO_4 \cdot 7H_2O$ has a limited market. It contains 2 to 3% moisture and has some storage and dumping problems. At Stora Kopparberg plant, the heptahydrate crystals were stored in the open, inside covered steel bins. Crystallization of heptahydrate requires cooling, and additional energy is required for refrigeration.

Stora Kopparberg, Domnarvet Steel Works, Borlänge, Sweden. In addition to treating WPL to obtain heptahydrate crystals, the wash water, vapor scrubbing water, and excess steam condensate are treated in a neutralizing plant at a rate of about 20 m^3/hr. After treatment iron is reduced to <2 ppm, TSS is reduced from 14 to <0.1 ppm, pH adjusted to 7.5 ± 1 with no unneutralized free acid in the waste. The sludge cake contains about 35% solid. The neutralized water is fed to 4 sedimentation tanks at the rate of 0.22 $m^3/m^2 \cdot hr$ with a residence time of 9 hr. Flocculent is added at the last tank.

The total production of 7000 tonnes/year of heptahydrate is completely utilized. A Swedish firm imports 15,000 tonnes/year of heptahydrate for water treatment.

Arbed Steel Works, Differdange, Luxembourg. This 100,000 tonnes/year continuous spiral sheet pickling plant was designed by Sundwig, of Germany, with the regeneration units designed by Falker, a Swiss company. About 1000 tonnes/year of heptahydrate crystals are produced by the refrigeration/crystallization/centrifuge technique. The crystals have only 1.1% water and 0.6% free acid and are primarily used for water treatment and algae growth prevention. Because of low requirements, it is also dumped in the slag yard.

The wash water is treated with milk of lime to pH 8 to 9, settled, decanted, and discharged to a river, and the sludge is deposited on the slag dump.

A new HCl pickling unit with regeneration was due to begin operation March 1979. The pickling unit was designed by Benguin (France) having a 25,000 tonnes/month capacity; the regeneration unit, using natural gas, follows the Keramchemie-Lurgi system.

Vöest-Alpine Aktiengesellschaft, Linz, Austria. No. 1 cold rolling mill uses H_2SO_4 pickling, and No. 2 cold rolling mill uses HCl pickling. The H_2SO_4 unit processes 600,000 tonnes/year and generates heptahydrate amounting to 12,000 tonnes/year using the Lurgi process. A small cut sheet plant in the No. 1 mill also produces 1200 tonnes/year of heptahydrate crystals. Most (90%) of the heptahydrate crystals go to the sinter plant and the rest for water treatment and as animal feed additive.

The No. 2 CR mill unit using HCl regenerates acid with the Ruthner design. The mill processes 800,000 tonnes/year and generates 3,600 tonnes/year of Fe_2O_3 for the ferrite industry. Wash water from No. 2 CR mill is neutralized. Sludge is transported by dump car for disposal, and the decanted water is run off to the Danube River. Wash water from No. 1 CR mill (H_2SO_4) is discharged to the Danubu directly.

ENSIDESA, Aviles, Spain. Of the two pickling lines, the H_2SO_4 line was installed in 1964, and the HCl in 1972. They are considering changing the H_2SO_4 unit to HCl. There is no acid recovery or neutralization plant. Between the two mills, the plant pickles 1.5 million tonnes/year. The WPL is mixed with wash water and fume scrubber waste and diluted to less than 1% acid concentration, conveyed by canal, and discharged to the ocean.

The plant has its own reservoir fed from the river and uses three water qualities in the plant. For all plant use, the industrial quality water is taken from the reservoir. There are filtering stations attached to each plant unit which treat the water and recycle some of it. Then the third system is the drinking water.

Hoogovens Ijmuiden BV, Ijmuiden, Holland. This large steel plant has a capacity of 6 million tonnes/year. It now produces 5 million tonnes/year and is planning to expand to 11 million tonnes/year. Only HCl pickling is used--two lines without regeneration and one line with a Lurgi regeneration plant. They had an H_2SO_4 line but changed over to HCl without regeneration. The waste acid and wash water is discharged to the sea for a fee paid to the government.

Table 4

WESTERN EUROPEAN STEEL PLANTS AND THEIR PICKLING PROCESSES

Steel Plant	Pickling Process
A. Sulfuric Acid Process	
1. Stora Kopparberg Dommarvet Steelworks, Börlange, Sweden	One continuous pickling line with $FeSO_4 \cdot 7H_2O$ as a by-product and H_2SO_4 recycling: Pickling capacity, 350,000 t/year. $FeSO_4 \cdot 7H_2O$ production in 1977--7000 tonnes. Price about $24/tonne. One-half of ferrous sulfate sold to water treatment plant and as flocculating agent. Other half sold to another company which burns off sulfur and mixes the oxide with fine ore and pelletizes/sinters. Small quantities used in concrete and to kill weeds.
2. Vöest-Alpine Aktiengesellschaft Linz, Austria	One continuous pickling line. Capacity--600,000 t/year. $FeSO_4 \cdot 7H_2O$--12,000 t/year, 90% to sinter plant, 10% for water cleaning and animal feed. One small cut sheet batch pickling unit. $FeSO_4 \cdot 7H_2O$--1,200 t/year.
3. ENSIDESA, Aviles, Spain	One continuous pickling line. Capacity--650,000 t/year. Waste pickle liquor (9-10% acid) diluted to less than 1%, discharged to sea via canal. Planning to install HCl line.
4. ARBED Steel Works, Differdange, Luxembourg	One continuous spiral pickling line. Capacity about 100,000 t/year. $FeSO_4 \cdot 7H_2O$--1,000 t/year, used for water treatment, also dumped in slag dump. New HCl line with regeneration under construction (March 1979).
B. Hydrochloric Acid	
1. Uddeholms Aktiebolag, Munkfors, Sweden	One continuous pickling line with acid regeneration. 1978 production, 20,000-25,000 t/year. HCl recovery, 97-99%. Oil consumption, 35 kg/h. Fe_2O_3 by-product, less than 1,000 t/year. Used in sinter. Some stored.
2. Fried, Krupp Hüttenwerke AG, Bochum, W. Germany	One continuous pickling line with acid regeneration. Capacity--1,200,000 t/year. HCl recovery about 98%. Fe_2O_3 by-product, 6,000 t/year, used in sintering plant.
3. Vöest-Alpine Aktiengesellschaft Linz, Austria	One continuous pickling line with acid regeneration. Capacity--800,000 t/year. Fe_2O_3 production--3,600 t/year, used in the ferrite industry.
4. ENSIDESA, Aviles, Spain	One continuous pickling line without acid regeneration. Capacity--850,000 t/year. Acid waste diluted with wash water and fume scrubber water to less than 1% and discharged into the sea.
5. Hoogovens Ijmuiden BV, Ijmuiden, Holland	Three continuous pickling lines; two older lines without regeneration, and one with regeneration. Now, as much as possible, waste liquor from older lines is regenerated in the double unit regeneration plant. Maximum capacity--1,500,000 t/year. Current capacity--1,100,000 t/year. Fe_2O_3 production about 6,000 t/year. Sold to ferrite industry. Quality very important. Bayer oxide--very good quality--sells for $500/tonne.
6. British Steel Corp. Ebbw Vale Works Ebbw Vale, U.K.	One continuous pickling line with regeneration. Capacity--1,400,000 t/year. Fe_2O_3 production about 12,000 t/year. Fluidized bed regeneration unit produced gray, coarse 100% >1/2 mm spherical particles well suited to sintering.

The No. 2 CR mill was built in 1971. The pickling line was designed by Wean-Dameron and the regeneration unit by Ruthner. Pickling about 1.1 million tonnes/year, the regeneration plant produces about 6000 tonnes/year Fe_2O_3 from the WPL. The Fe_2O_3 is used in the ferrite industry where the quality is very important. Chloride should be less than 0.1%; density (after settling) 0.8 g/cm^3; specific surface, 270 to 320 m^2/g; loss on ignition, 0.3% at 800 C. A very high quality oxide, such as that produced by Bayer, sells for $500/tonne.

The wash and fume scrubber water is partially used for LD (BOF) gas cleaning. The rest of it is mixed with NaOH and discharged 1 to 2 km out into the sea. For the month of May 1978, the range of flow was 40 to 580 m^3/hr, well under the limit of 1000 m^3/hr. The pH ranged 6.8 to 8.5, TSS 16 ppm avg (5-375 ppm, range), under the 30 ppm limit. Iron limit is 3 ppm, and soluble iron average was 0.34 ppm.

Government regulations limit waste acid discharge to the ocean to a rate of 170 m^3/day (30 gpm), amounting to 22 tonnes of Fe^{++}/day. Other limitations are 2.9 tonnes HCl/day and 7 kg Cu/day. In addition, a penalty equivalent to $1.30/ton of F^{++} is charged when the limit is exceeded.

British Steel Corporation, Ebbw Vale Works, Ebbw Vale, U.K. The three H_2SO_4 pickling lines were shut down in 1974 and replaced by one continuous HCl line to treat about 1.4 million tonnes/year and to regenerate acid in a Lurgi-designed fluidized bed roaster. The pickling line is designed by Head Wrightson. Fe_2O_3 production amounts to 12,000 tonnes/year, and the coarse (>½ mm) gray particles are excellent as sinter feed. Loss of pickling is about 0.6%. The WPL contained 3 to 6.5% HCl and 90 to 122 g/l iron. Rinse water contained HCl 20 g/l and Fe 10 g/l. The Fe_2O_3 had a 0.075% chloride content. All wash waters are properly treated, and the effluent discharged into the Eddw River goes through the Bristol Channel to the sea, 32 km (20 miles) away.

Fried. Krupp Hüttenwerke AG, Bochum, West Germany. The plant has two HCl regeneration units; the first one designed by Dr. C. Otto is not giving satisfactory operation now. The second one designed by Keramchemie is mostly used to treat WPL at the rate of 3000 l/hr (13 gpm). It is fired by coke oven gas at the rate of 1400 m^3/hr. Fe_2O_3 produced at 6000 tonnes/year is used in the sintering plant. The wash water is neutralized with lime water (pH 7 to 8), stirred with air, sent to settling tanks, and then filtered and the cake is dumped. The effluent is discharged at the rate of 20 to 40 m^3/hr. New water purchased for pickling costs DM 0.95/m^3 ($2.00/1000 gal).

Ruhrverband, Essen, West Germany; Emschergenossenschaft, Essen, West Germany. In the Ruhr district in West Germany, where industry is highly concentrated, separation of municipal and industrial waste waters is encouraged. Central treatment plants for each waste stream permits special water treatment techniques with the additional prospect of metal recovery and recycle. All plants in this area are members of the Ruhrverband and pay for water use. The Ruhr is a drinking water river. Some 100 water treatment plants are located in this area.

In addition to steel plants, there are many coal mines which generate a lot of coal fines entrained in wash water amounting to 800-1000 tonnes/day of coal. These coal fines mixed with steel plant wastes and biological wastes combine to form a sludge having a combined carbon of 40%, which is used in power plants equivalent to brown coal. In a recent U.S. EPA trip report,[22] Craig has mentioned the concept of waste exchange which has been successfully implemented in Europe.

Emschergenossenschaft (Emscher Association) was created in 1904 to control all water discharges in the Emscher River basin. Recently, in order to reduce the load on the Rhine, a large-scale treatment plant was built at Emscher, 7.5 km from the Rhine confluence. It serves a population of about 2.5 million and can handle a maximum flow of 30 m^3/sec. The sludge produced here is burned in the Karnap Power Station of the RWE AG.

Centralized treatment plants for industrial wastes, both publicly and privately owned, treat the wastes of their member companies on a fee basis. The Altena Central HCl regeneration plant (30 members) recovers HCl from WPL and sells the Fe_2O_3 to use as a land fill.[22]

Ferrous Sulfate Heptahydrate (Copperas), Production and End-Use

The 33 plants recovering copperas are given in Tables 2 and 3. Only one of them, Bethlehem's Lackawanna plant, is an integrated steel plant. It is possible that they are using a modified KSF process with 5 modular units each capable of processing 19 l/min. In all, there are about 32 modular units processing 570 l/min of WPL by the KSF process. On an average, about 105 liters of WPL is formed on treating 1 tonne of steel resulting in 30 kg of copperas crystals at 0.6% iron loss. With a total processing capacity of 570 l/min, copperas production rate from all KSF units will amount to about 160 kg/min or about 10 tonnes/hr. The actual annual production will depend on the number of shifts operating. Assuming a standard 2-shift operation of 16 hr/day and 330 days/year, the total copperas production from all KSF units can be estimated at about 55,000 tonnes/year.

The three plants using vacuum crystallizing Keramchemie process have a combined capacity of 114 l/min of WPL and may produce as much as 10,000 tonnes/year of heptahydrate on the basis of continuous 3-shift operation.

The batch-type Crown Chemical process treats 42 l/min of WPL and on a 2-shift/day, 330 days/year may produce about 4000 tonnes/year of the heptahydrate.

The total $FeSO_4 \cdot 7H_2O$ (copperas) production from the 28 plants at present may amount to as much as 68,000 tonnes/year, if fully operated.

The four Pureco process plants treat a total of 80 l/min of WPL and produce about 10 kg/min of $FeSO_4 \cdot H_2O$--the monohydrate. The Pureco process is continuous, and if operated on the basis of 20 shifts/week and 50 weeks/year for a total of 8000 hr, it will produce about 4800 tonnes/year.

The single Sulfex process unit treats 35 l/min of WPL and, on 8000 hr continuous basis, is capable of producing 2300 tonnes/year of $FeSO_4 \cdot H_2O$.

The total $FeSO_4 \cdot H_2O$ (monohydrate) produced from the five units may amount to 7000 tonnes/year. Thus, a total of about 75,000 tonnes/year of ferrous sulfate crystals (copperas 68,000 tonnes and monohydrate 7000 tonnes) are available in the market for use or disposal.

Approximately three times more H_2SO_4 is needed than HCl to pickle one tonne of steel on a 100% basis. On this basis, in 1974 the estimated 30 H_2SO_4 pickling lines in the steel industry treated about one-third of the total estimated 60 million tonnes pickled, or about 20 million tonnes. At 0.6% iron loss, this amount of steel treated will generate about 600,000 tonnes/year of heptahydrate (60 lb/ton of steel) if fully recovered. To this amount, about 12 to 15% may be added if recovered fully from the secondary and tertiary processing plants spread all over the U.S.A. Thus in 1974, the total potential for heptahydrate production could have been estimated to be as high as 680,000 tonnes/year. Using the 2% growth rate projections, by 1985, the amount of steel pickled may increase to 72 million tonnes/year. If the additional pickling capacities added maintain the same ratio between H_2SO_4 and HCl pickling tonnage (1:2), then the total potential heptahydrate generation may increase to about 800,000 tonnes/year by 1985, about ten times the amount that is currently processed. That is the potential magnitude of copperas that must be either safely dumped, or normally absorbed in the marketing process which is preferred.

Besides steel plant pickling, there are other industrial processes which generate ferrous sulfate heptahydrate. These are (1) commercial producers who deliberately dissolve scrap in sulfuric acid to produce the salt, (2) a by-product from titanium pigment producing units, and (3) from sulfuric acid leaching of copper-bearing minerals and slags. The five major commercial producers have a total copperas capacity of 320,000 tonnes but produced only about 180,000 tonnes in 1967 and were projected to produce as much as 270,000 tonnes by 1975.[23] The two largest producers are National Lead Company and Pfizer, Inc., with a total installed capacity of 250,000 tonnes/year. Thus, there exists a large surplus commercial capacity for production of copperas. The average price of commercially produced copperas remained about $5 to $6/tonne during 1960 to 1967.[23]

Ferrous sulfate heptahydrate has been used for a long time for production of synthetic iron oxide pigment, copperas red. In a 2-step heating process, the sulfurous off-gas can be used to generate H_2SO_4. A wet chemical process by Penniman and Zoph is also used to produce synthetic iron oxide from heptahydrate solution.

Iron oxides used for pigments and electronics can be produced as a by-product from the titanium dioxide pigment industry.[15] The sulfate-process portion of the titanium pigment industry has so far been a key source of copperas. A shift in titanium pigment technology from sulfate to chloride process will decrease copperas production, but iron oxide may be available as a by-product if $FeCl_2$ is converted to Fe_2O_3. Apparent domestic demand of iron oxide pigments have seen a steady growth of 45% between 1964 and 1974. The compounded growth rate of 3.6%, if projected to 1985, indicates a total domestic demand exceeding 250,000 tonnes valued at $150 million (U.S. $0.30/lb).

The market share of copperas from all sources has been estimated at 55%, iron oxide pigments; 30%, ferrites; 5%, water-sewage treatment; and 10%, others including fertilizers, feed stock, ink, etc. While innumerable end uses are available, most of them are small. Two major consumers are paint and plastics. Sales of paints and allied products increased from $2.4 billion to $3.6 billion from 1963 to 1971. A $7 billion market is projected in 1980.[24] The plastic resin market doubled during the same period and is projected to reach $12 billion by 1980.[24]

A trend in automotive finishes to the copper and bronzes has created a market for ultrafine iron oxides referred to as "transparent" or "low opacity" pigments. These pigments are combined with aluminum to produce metallized automotive finishes.[25] The present market is estimated to be between 1500 and 2500 tonnes/year, worth about $5 million.

Utilization of the additional property of absorbing ultraviolet radiation is being investigated to determine the potential of transparent oxides in containers and packaging for food and wherever else durability, transparency, and ultraviolet absorption are desired in a pigment.[15]

Steel plant WPL oxides (from $FeCl_2$) are displacing some of the copperas oxide products from the traditionally ferrite market. The soft ferrite market still remains a large consumer of copperas reds and calcined yellow oxides. For 1972, the estimated shipments of permanent magnets, T.V. yokes, memory cores, and ferrite parts were $192 million,[26] and they are expected to grow significantly. A world ferrite production of 495,000 tonnes/year is estimated by 1985.[27]

At present, only a very small fraction (5%) of copperas is used for water-sewage treatment. The result of a study made by the Fitzsimons Steel Company, Youngstown, Ohio,[23] in 1973 to market heptahydrate for sewage-water treatment in 13 communities within a 120 km (75 mile) radius was not encouraging. For coagulation, alum is usually preferred and the water treatment plants were unwilling to try new products. Where phosphate control is important, copperas is desirable but must compete with $FeCl_3$. Detroit receives WPL free from HCl pickling plants of Great Lakes Steel Company and Ford Motor Company. Milwaukee uses $FeCl_3$ but has started to use copperas. Chicago uses $FeCl_3$ plus some ferric sulfate. They found WPL from local mills too unpredictable and impure for safe usage.[23]

On the other hand, a more recent experience of Bethlehem Steel Plant, Sparrows Point, Maryland, is more encouraging.[28] The 6.3×10^6 tonne/year plant generates about 100,000 gallons of WPL per day. They have successfully used this WPL for removing phosphorus from municipal wastewater at the City of Baltimore's 700,000 m^3/day (185 Mgd) Back River wastewater treatment plant and at the District of Columbia's 1.14×10^6 m^3/day (300 Mgd) Blue Plains sewage treatment plant.

There is no doubt that in phosphate treatment, WPL and copperas--supplied in proper condition, and with some treatment plant modifications, such as addition of solution tank, aeration facilities, and larger pumps--can adequately compete with its close rival, $FeCl_3$. With the emphasis on secondary and tertiary water-sewage treatment, the market share of copperas should grow significantly from the present 5%. And even a small increase, when treating billions of gallons daily, amounts to a lot of WPL-copperas use potential.

While worthwhile and economic end uses for recovered copperas crystals will be desirable, it must be recognized, at present, that there does not exist a large market for copperas and the market has to be created. During this period of market development, the copperas produced from WPL can be handled in a far more effective way (environmentally speaking) than the present techniques of contractor hauling, neutralization/lagooning, or deep-well disposal of WPL.

The essentially acid-free copperas crystals can be dumped on municipal dumps as proper fill material. They may be combined with other municipal incinerator inert products and then dumped.

The crystals can be mixed with lime, and less lime quantity will be needed because there is no free acid to neutralize. Or, the ferrous sulfate can be converted to magnetic oxide and calcium sulfate with lime and oxidation, and the inert matter can be used as a landfill.

WHAT'S IN THE FUTURE

The bulk of copperas is not, at present, generated at the integrated steel plants, but in the hundreds of secondary steel processing plants. Titanium pigment manufacturers and the commercial producers also generate a significant quantity of copperas. While these plants are dispersed all over the U.S.A., they are, to a certain extent, clustered in certain industrially developed regions, for example, the Chicago-East Chicago-Gary greater metropolitan area. Before trying to solve the problem of disposal of copperas yet to be generated from steel plant WPL, it will be necessary to direct attention and effort to make use of WPL from the secondary processing industries to generate copperas, and either to find a market for it or to dispose of it in an environmentally safer way. To achieve this end, it will be necessary to direct attention to the following:

1. A study to define the scope and establishment of regional, centralized WPL facilities to be funded jointly by the secondary processors and aided by EPA or a similar regulatory body for initial subsidized operation.
2. Co-treatment of different waste streams to recycle and recover valuable products. Also, to develop waste exchange information data with the help of EPA to aid industry in this effort.
3. Promotion of tertiary sewage treatment with particular emphasis on phosphate removal. Also, to establish an EPA directive to require all EPA-aided sewage treatment facilities to utilize recycled waste product such as copperas and to extend additional aid to them for necessary equipment modifications to make such use possible.
4. Research and development to find new uses for copperas, to improve pickling technology, to reduce use of acid and water, and to minimize iron loss resulting in process development with zero liquid discharge (KSF or similar process).

Centralized WPL Treatment Plant

The economics of scale will be very favorable for such a treatment plant. Similar treatment plants are in operation in West Germany serving industries within a radius of 80 km. The mechanics of joint ownership and Federal aid must be studied in the U.S. economic and regulatory context. However, a radius of 80 km will encompass the whole of the Greater Chicago Metropolitan Area and beyond. At some point in time, some of the big steel industries of this area using H_2SO_4 acid pickling may even participate in its operation. The members will be charged on the basis of WPL volume treated, and a credit will be given for recovered acid. The heptahydrate will either be sold to sewage treatment plants of the same area operated with Federal aid, or converted to oxide, or treated and dumped as land fill.

Well-established technology for WPL treatment for copperas production is now available (one being the KSF-zero discharge process). Nonetheless, new research and development studies are needed to develop alternative economical processes. The Crown Chemical ion exchange process[3] has demonstrated a marketable Fe_2O_3 starting with heptahydrate crystals. Using a double loop counter current flow, a hydrogen ion exchange resin, nitric acid, and a hydrolyzer, a bench scale unit produced ferrite/pigment grade Fe_2O_3. In 1975, about 17,500 tonnes of Fe_2O_3 were produced from steel plant WPL and sold at an average cost of $55/tonne, principally to ferrite manufacturers. A demonstration plant based on the hydrogen ion exchange resin process will be required before the economics of the process can be established.

There are many other areas where additional research will bear results. For example, several laboratory-scale electrolytic techniques have been developed, but none has attained a demonstration plant stage. It was demonstrated that using Hg cathodes, electrolytic regeneration of iron is both reliable and economical.[29]

Co-Treatment of WPL and Other Waste Streams

WPL is still treated with technologies 50 years old: cooling, crystallization, filtration, washing, drying heating—a combination of fairly primitive technologies. Very little attention is given to advanced technologies such as ion exchange, electrolysis, high-intensity magnetic separation, and reverse osmosis, to name a few. Many other metal processing industries generate waste liquor/solids which are equally or more difficult to handle. Electroplating and electronic industries are two such groups whose waste streams may be effectively co-treated with WPL to benefit both.

Two printed circuit (PC) shops are presently using heptahydrate to treat electroless copper and alkaline etch rinses. A large West Coast PC manufacturer treats 1200 l/day with 5 to 20 g/l of heptahydrate. An East PC manufacturer treats six electroless copper rinses and one alkaline etchant rinse with heptahydrate in a continuous flow system. The 100 l/min (26 gpm) flow of 20 to 30 mg/l copper is reduced to less than 1 mg/l after the sulfate treatment. Copper plating rinse waters were treated with WPL to reduce initial copper concentration of 1000 mg/l to 0.5 mg/l.[30] A similar co-treatment of chromate waste water with WPL and wash water can reduce iron and chrome in the final effluent to 0.5 and 0.05 mg/l, respectively.[31]

While recovery and recycling of acid and metallic values are worthwhile under certain conditions, it is often necessary to treat WPL and acid wash water with a neutralizer to make it environmentally harmless. Often, lime is used—a highly energy-intensive product. On the other hand, a large quantity of lime residue is available from the carbide process. Like many unwanted waste products, the lime residue has a negative value and, instead of lime, this lime residue can be effectively and economically co-treated with wash water/WPL.[32]

In addition to development of co-treatment process technology, it will be very desirable to compile regional/local waste stream/solid waste generation information. This information can be made available to the regional industries with available technological information regarding the possibilities of their co-treatment and disposal. A Federal agency such as EPA may select one large region (for example, the Chicago area) as a target area to initiate this study. This pattern of waste information exchange was initiated in West Germany, and now the industries have developed their own contacts and need very little federal help.

Tertiary Sewage Treatment and Phosphate Removal

Potentially, sewage treatment for phosphate removal and water treatment for coagulation are two uses which can theoretically utilize all possible copperas (or WPL) production. However, long-term agreements, reluctance by authorities to experiment with new chemicals, lack of compelling enforcing regulations for phosphate removal, additional expense for equipment modification, and, lastly, no concerted expression of interest from different Federal authorities for recycling of heptahydrate are some of the major reasons for the poor share (5%) of heptahydrate usage in water-sewage treatment. Because the potential is so vast and the application of copperas is technologically so straightforward, economical, and well-proven,[28,33] it is surprising that the Federal authorities who aid many of the urban water-sewage treatment plants did not yet exert their influence to promote the use of copperas in this application. The existing Federal regulations which reward use of recycled products can be effectively utilized in water-sewage treatment plants. The aid to these plants can be made contingent on their utilizing recycled products such as copperas or WPL. Additional aid may be available to these plants for equipment additions and alteration which will be required if copperas is used to replace $FeCl_3$ and alum. This use is potentially most effective because of the close proximity of the copperas (WPL)-generating industries and the local treatment facilities, thereby reducing transportation cost very substantially.

Research and Development of Pickling Technology

While pickling is an old technology, many changes have taken place during the last 20 years to improve its application. One major shift is from H_2SO_4 to HCl pickling resulting in a better looking product, faster pickling, and potential for easier HCl regeneration and by-product iron oxide production and usage. After a rapid growth of HCl pickling, it has come to a balance with H_2SO_4 pickling on a tonnage basis of 30% H_2SO_4 to 70% HCl. Further, HCl pickling conversion of existing H_2SO_4 pickling lines has virtually ceased in the U.S.A., whereas it is still proceeding in Europe. The higher HCl cost relative to H_2SO_4, and the possible oversupply of H_2SO_4 because of SO_2 emission control and S recovery due to EPA regulations may stabilize H_2SO_4 cost farther, thereby reversing the trend of HCl acid pickling. Any new green-field plant is likely to use HCl pickling, but the additional rounding-off facilities to existing units will still be by the H_2SO_4 acid process where already existing, and will add to the copperas disposal problem.

New pickling technology using a mixture of H_2SO_4/HCl acids has been developed by Wean/KSF[5] and has been tried in continuous/batch pickling operation. HCl assists H_2SO_4 in the pickling, and H_2SO_4 also acts as a reagent regenerating HCl from $FeCl_2$ according to the equation:

$$FeCl_2 + H_2SO_4 \rightarrow FeSO_4 + 2HCl$$

Copperas can be recovered from the WPL with little chloride contamination. The resulting pickled steel has the brightness of HCl pickling.

Additional studies are required in the area of pickling mechanism and washing of pickling solution from the sheet surface. If a true understanding of the mechanism involved in the pickling of steel by HCl and H_2SO_4 is obtained, a new technology using less acid and consuming less iron can be realized. Generally, at 0.5% Fe loss, one tonne of steel pickled produced 25 kg (55 lb) of $FeSO_4 \cdot 7H_2O$. At 1% Fe loss, it is 50 kg of heptahydrate/tonne steel. While these are average values, different products, depending on their surface area/volume ratio and process technology, will show different amounts of iron losses. The data show that in wire pickling about 1% iron loss is encountered, whereas in billet pickling it is only 0.22%.[21] Thus, any effort in understanding the mechanisms involved in iron loss and the effect of inhibitor control in minimizing iron loss will eventually have the highest potential effect in reducing copperas production. The industrywide figure is 0.6% Fe loss, and a reduction to 0.5% Fe loss means a total reduction of 16% in WPL/copperas production amounting to hundreds of thousands of tonnes per year.

Considerable improvement in the technology of washing of steel surfaces has taken place in recent years. The traditional method of dipping in water bath and flood cooling requiring vast amounts of water is giving way to more scientific spray cooling and temperature control. Also, indirect heating of baths and external heat exchangers are lessening steam condensation and dilution effects of earlier days. However, the mechanisms involved in the removal of thin acid/water films (water is a polar compound) from a freshly pickled and highly reactive steel surface as a function of water temperature, velocity, and other undefined parameters are not adequately understood. Also, additional equipment development in squeezing out carry-over acids will tremendously help in reducing wash water problems and its subsequent disposal.

New research to expand the use of copperas in new areas is greatly needed along with effort to hold the market for existing uses. For example, the introduction of the Aniline Process for making iron oxide pigment is likely to affect pigment use of copperas and must be countered by research.

CONCLUSIONS AND RECOMMENDATIONS

At present, the integrated steel industry does not feel the economic compulsion for generating copperas from the several hundred million gallons of waste pickle liquor it produces annually. As such, copperas from the steel industry does not pose any problem to those who are trying to market it. Copperas has a ready but limited market. The largest user is the pigment industry, and it cannot possibly absorb significantly larger quantities in the near future. The most promising area for expanded use is sewage treatment for phosphate removal. The long-term contracts and traditional resistance to use of an unknown chemical is, at present, preventing its effective utilization. Also, lack of emphasis on tertiary treatment regulations and positive incentive in the form of additional federal aid for equipment modifications and use of recycled products are several institutional factors holding back increased used of heptahydrate in sewage treatment.

Even if heptahydrates are not all marketable they are better for disposal than diluted and neutralized waste liquor. To economically achieve copperas production, large centralized treatment units such as those that exist in West Germany will go a long way in solving the problems of hundreds of small processing units. Also, research studies are needed on co-treatment of different waste streams, and regional surveys are needed to bring such information to the attention of companies interested in waste treatment facilities.

Sulfuric acid pickling in the steel industry is anticipated to continue to make up about thirty percent of pickling practice. New plants are likely to use hydrochloric acid pickling combined with acid regeneration in spite of the fact that the process is energy intensive. The rounding-off facilities to be added to steel plants is likely to extend the existing pickling practice. If new regulations force some of the steel plants to switch from deep-well disposal, neutralization/lagooning, or discharge into large water bodies, then the plants may consider heptahydrate production as one of the alternatives. At present, only 75,000 tonnes of iron sulfate crvstals are produced and most of the product is marketed.

The bulk of marketed copperas is not generated at the integrated steel plants which process about 20 million tonnes of steel per year using sulfuric acid. If it were, then an additional 600,000 tonnes/year would be added to a market which does not have an easy time in marketing the estimated 75,000 tonnes/year produced by the small steel processing units. Under some future altered circumstances, production of copperas from waste pickle liquor by the integrated steel plants has the potential of adversely affecting the copperas market. In order to avoid serious future dislocation and to promote use of copperas (and WPL) and expand its market in a positive manner, several suggestions are made below:

1. A study to define the scope for establishment of regional centralized waste pickle liquor facilities to be funded jointly by the secondary processors. Encouragement, and perhaps initial subsidized operations, from government may be needed.

2. Significant research on co-treatment of different waste streams and on solids to recycle/recover valuable products and to stabilize the waste for safe disposal. Establishment of a bank of waste exchange information on a zonal basis for different regional industries to take mutual advantage of one another's waste products.

3. A study of the use of spent pickle liquor and copperas for wastewater treatment, particularly tertiary treatment for phosphate removal and effluent polishing. This approach uses two environmentally negative practices, the disposal of spent pickle liquor and the discharge of phosphorus, to abate each other. The advantages and disadvantages should be considered, including the problem of heavy metal contamination of wastewater treatment plant effluents and sludges, and the question of whether spent pickle liquor should be used directly or only the copperas derived from it. Methods of encouragement should also be considered.

4. Research and development to find new uses and to extend present application of copperas by improving its quality. New studies are needed to improve pickling technology so that less iron is lost, resulting in less WPL. Additional knowledge is needed regarding mechanisms of pickling and the mechanism of washing of drag-out acids with minimum water.

ACKNOWLEDGMENT

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THE EFFECTS OF PRETREATMENT ON COKE PLANT WASTE WATER BIOLOGICAL TREATMENT SYSTEMS

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The United States Steel Corporation in conjunction with the Environmental Protection Agency is conducting an extensive experimental program to develop input data relative to BATEA technology for coke plant waste waters. The program which involves testing on both a bench scale as well as the pilot scale is concerned with determining the optimum operating criteria for coke plant biological treatment systems. Once the optimum conditions are identified, further investigations will evaluate the impact of the addition of powdered activated carbon to an optimized system.

As an initial step in identifying optimum operating conditions, a separate investigation was conducted to evaluate the importance of precleaning of the feedwater to the biological system. The evaluation program centered on those constituents falling into the two general categories of suspended solids and "oil and grease". Various removal techniques were evaluated and the necessity for achieving specific levels of influent pretreatment was addressed. The validity of the resultant conclusions relative to precleaning is supported by operational data from a 9,500 m^3/day (2.5 MM GPD) coke plant waste water treating facility.

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THE EFFECTS OF PRETREATMENT ON COKE PLANT WASTE WATER BIOLOGICAL TREATMENT SYSTEMS

BACKGROUND AND INTRODUCTION

Clairton Works of the United States Steel Corporation is one of the world's largest producers of metallurgical coke. The facility consists of nearly 1,000 ovens which produce sufficient quantities of coke to supply all of the corporation's steel-making facilities in the Pittsburgh area with some excess being available for other corporate locations. In addition to producing coke, Clairton Works has a totally-integrated system for recovering and refining a full complement of coal chemicals. Unlike traditional by-product facilities which utilize a series of low pressure recovery processes, the Clairton system employs elevated pressures 3.52-3.87 Kg/CM^2 (50-55 PSIA) and unique separation and recovery processes. Naturally-occurring ammonia is recovered as an anhydrous product using the U. S. Steel patented Phosam process. Light oil fractions are separated from the gas using a computer-controlled cryogenic-regenerator system in which the gas is cooled to temperatures of less than -157° C (-250° F). This same regeneration system yields an ultra-pure, hydrogen-rich gas for consumption in the synthetic ammonia plant while simultaneously providing a feed gas of exceptional quality to heat the coke ovens. Additional facilities are operated for the removal of sulfur from fuel gases leaving Clairton Works for use in other local U. S. S. facilities. In addition to the primary-recovery facilities, complimentary systems are operated to produce metallurgical grade anhydrous ammonia, benzene, toluene and xylene as well as a complete line of tar based derivatives and naphthalene.

At typical operating levels, Clairton Works generates somewhat in excess of 9,500 m^3/day (2.5 MM GPD) of contaminated water. Approximately 45% of the total generation occurs as a direct result of the coking operations with the remaining 55% attributable to chemical processes. The typical composition of the raw contaminated water is shown in Table 1.

Table 1

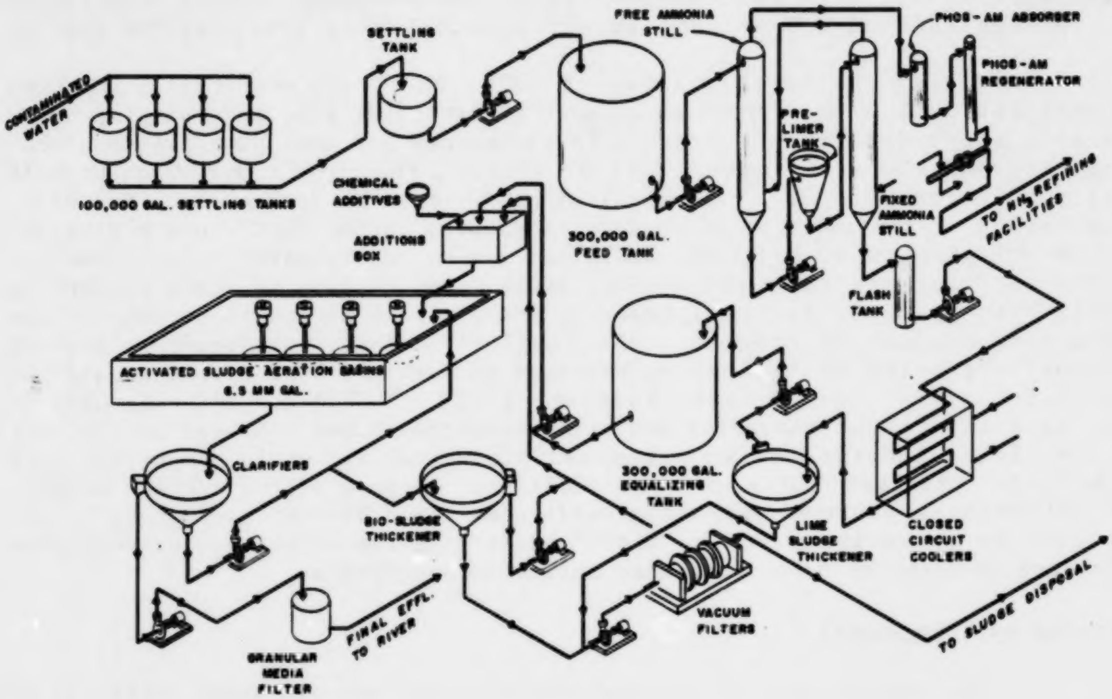
COMPOSITION OF COKE PLANT CONTAMINATED WATER

Ammonia	**— 1500-2000 PPM**
Phenol	**— 800-1200 PPM**
Thiocyanate	**— 600 - 700 PPM**
Cyanide (Total)	**— 200 - 400 PPM**
Oil/Grease (Freon Extractibles)	**— 2000-4000 PPM**
Total Suspended Solids	**— 300-1500 PPM**
pH	**— 8-9**
Temperature	**— 130-170° F.**

The principle elements of the Clairton Works contaminated water treatment facilities are shown schematically in Figure 1. Following gravity separation of both solids and suspended oils in the settling tanks, the contaminated water is processed through the U. S. Steel patented Cyam process. Here the water steam stripped of so-called "free ammonia", pH adjusted by the addition of lime to liberate "fixed ammonia" and finally further steam stripped to yield a biological feed stream of desired ammonia content. In addition to ammonia removal, the Cyam system also accounts for the removal of 90-95% of the cyanides as well as other "acid" gas fractions. Following ammonia removal, the water is cooled and clarified prior to biological treatment. Clarification is provided by the use of a conventional center-well peripheral overflow clarifier.

Figure 1

United States Steel Corporation - Clairton Works
CONTAMINATED WATER TREATMENT PLANT



The biological treatment system is a single-stage process consisting of 2 independent aeration basins operating in parallel. The total system volume is in excess of 24,600 m^3 (6.5 million gallons) with aeration and mixing being provided by low speed mechanical surface aerators.

Concerns relative to the impact of influent quality on the overall performance of a biological system arose as a result of studies to determine the ability of the existing system to meet proposed 1984 final effluent standards. A literature search substantiated by in-plant inspections of operating facilities suggested that technology developed in the petroleum industry[1] might well have validity in the coking industry. This technology stressed the importance of extensive precleaning of the feedwater to a biological system as a significant prerequisite to achieving nitrification. Total suspended solids and oil/grease concentration each not exceeding 20 mg/L were stated as constraints. Because of the qualitative similarities which exist between coke plant waste waters and refinery waste waters, consideration was given as to the applicability of this technology. In-plant investigations conducted on what might be termed a "macro" level concluded that although coke plant water contained the same general spectrum of contaminants as refinery wastes, the use of the previously stated constraints concerning TSS and O/G did not appear applicable to the Clairton system.

During the third quarter of 1979, the Environmental Protection Agency and U. S. Steel agreed to conduct an extensive experimental program to develop input data relative to BATEA technology for coke plant wastewaters. the goals of the study were twofold. First, the conditions which promote optimum performance of a biological system were to be determined. Secondly, the impact of the addition of powdered activated carbon (PAC) to a biological system operating at the optimum conditions was to be evaluated. Environmental Dynamics Incorporated of Greenville, South Carolina, was selected to work in conjunction with U. S. Steel Research and Clairton personnel to conduct the year-long evaluation program. The complete investigative program involves extensive testing of biological reactors on both the bench-scale as well as the pilot scale. Bench-scale reactors [.028 m^3 (7.5 gal.)] being used to evaluate individual variables and pilot reactors [3.2m^3 (850 gal.)] used for a parallel evaluation of an optimized biological system in comparison to a similarly optimized system with PAC addition. As part of the overall program of determining optimum operating conditions for a biological system, it was decided to investigate (on a "Micro" basis) the importance of influent precleaning in terms of total suspended solids and oil/grease.

METHODS AND PROCEDURES

The evaluation of pretreatment alternatives was based primarily on jar tests. The limitations of using a batch procedure like the jar test to evaluate a continuous-flow treatment unit was recognized. It was felt, however, that since alternatives were being compared, the results would be relative, and the procedure could be used to define optimal conditions. To minimize the analytical load generated by the large number of jar tests, qualitative observations such as floc size, supernatant clarity and relative settling rate were used to screen alternatives. When promising alternatives had been defined, quantitative analyses of the supernatant oil and grease and suspended solids were used to define the optimum conditions.

An evaluation of the existing lime sludge thickener (LST) was included in the pretreatment evaluation. To define the performance potential, several Class 2 settling analyses were performed[2]. This procedure, designed to predict clarification of flocculent suspensions, consists of quiescent batch-settling tests with periodic measurement of suspended solids at several depths in the subsiding column. The concentrations at the various depths and times permit the development of the relationship between overflow rate and solids removal. Such tests were conducted to estimate performance under three different coagulant schemes.

In addition to optimizing the performance of the LST, alternative pretreatment processes were considered. The dissolved air flotation (DAF) process was evaluated using a batch pressurization tank and separation column. By varying the pressure and volume in the pressurization tank, it was possible to investigate a wide variety of air-to-solids ratios. Additional tests were also conducted to evaluate the applicability of the induced air flotation (IAF) process.

Granular-media filtration was considered as a supplemental process to upgrade the effluent from the LST. A 5 cm (two-inch) diameter, dual-media filter was used in the evaluation. The media consisted of 30 cm (12 inches) of 0.9 mm anthracite and 30 cm (12 inches) of 0.65 mm of quartz sand over 9 cm (3-1/2 inches) of graded gravel. The length of the filter run was determined by the available head of 1.2 m (4 feet) or the breakthrough of solids in excess of 20 mg/L. Performance of the filter was assessed by effluent solids and oil and grease levels.

RESULTS AND DISCUSSION

Oil and Grease Removal

In this study, the term "oil and grease" is used to refer to those materials which are extractable in fluorocarbon-113 and detectable by gravimetric analysis after evaporation at 70° C. The nature of the test, then, limits its applicability to higher molecular-weight hydrocarbons which have boiling points greater than 70°C. This is a reasonable limitation when using the test to assess the impact of oil and grease on the operation of biological processes since the lower molecular-weight hydrocarbons, which are not detected in the test, tend to be more degradable and have little adverse impact on the process. One group of lower molecular-weight compounds which the test does measure is the organic acids. These compounds are normally dissociated and, therefore, soluble at typical coke-plant waste water pH. During the oil and grease extraction, the pH is first lowered to less than 2.0 which shifts the ionic equilibrium resulting in most of the acids being non-dissociated and extractable. The oil and grease procedure, then, measures a class of compounds which are normally soluble. When using the freon-gravimetric test to monitor influents to biological processes, high influent levels and potential operating problems can be indicated when large quantities of organic acids are present. These acids, in general, are biodegradable, which would preclude any adverse impact on the biological process.

One of the goals of the Clairton BATEA study was to optimize the existing biological process to determine what, if any, further improvements would be required to meet future standards. Similar studies in other industries[1,3,4] have indicated that operation at long solids retention time (SRT) results in the enhancement of effluent quality. Successful operation at long SRT, however, requires an influent which is low in oil and grease since higher molecular-weight hydrocarbons are normally removed by physical absorption on the sludge rather than biodegradation. These materials, therefore, accumulate at long SRT resulting in deterioration of settling characteristics and eventual process failure. In light of this background, an influent oil and grease target of 20 mg/l was selected for the pretreatment studies.

Jar tests were used to evaluate the effects of a wide variety of operational variables on the removal of oil and grease by the existing pretreatment units. These tests indicated that the presently used polymer and dosage performed as well as alternative coagulants or coagulant-flocculant aid combinations. Varying the coagulation pH from 8 to 12 and the provision of up to eight minutes of supplemental flocculation also failed to provide improvements over the existing scheme. In general, the supernatants produced in jar tests with optimum coagulant addition were similar to LST effluent in oil and grease content indicating the near-optimal performance of the existing system.

The failure of the jar-test program to indicate a potential for significant enhancement of LST performance for O/G removal led to the evaluation of alternative processes. Batch DAF studies showed that the density of the solids and Freon extractable materials in the LST feed were such that flotation would be very difficult. No single polymer was able to produce flotation; and, although several coagulant combinations resulted in flotation, the supernatant quality was poorer than the existing LST effluent. One combination consisting of a cationic primary coagulant and an anionic flocculant aid proved effective, but the dosages required were economically prohibitive and the float volumes excessive. The test results indicated that flotation was not a viable option for pretreatment of coke plant wastewater.

The final alternative for attaining the oil and grease target of 20 mg/l was the use of granular-media filtration as a supplement to the existing LST. In these tests, LST effluent, which had been treated with the optimum polymer dose prior to settling, was passed through a laboratory-scale sand-anthracite filter. The results of the filter runs summarized in Table 2 indicate very little removal of oil and grease with the effluent far in excess of the target.

Table 2

SUMMARY OF BENCH-SCALE FILTRATION TESTS

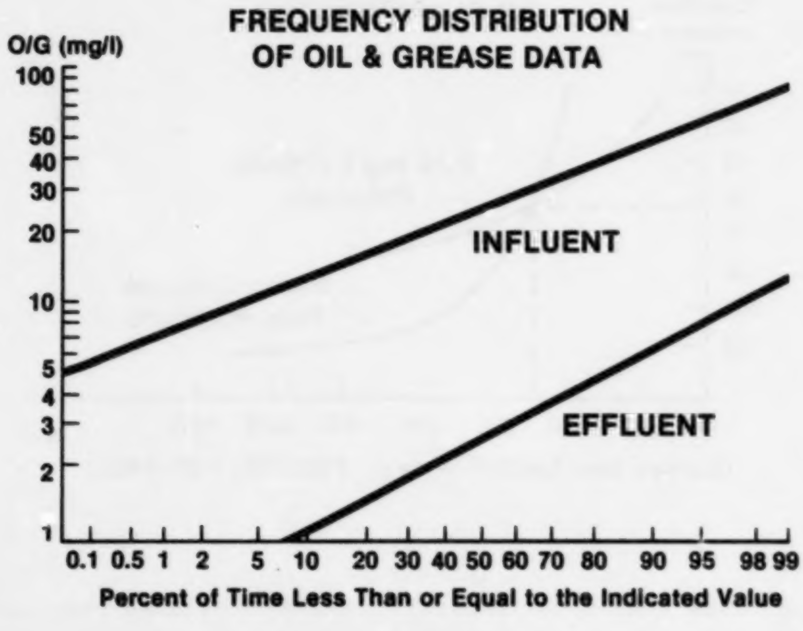
					AVG. TSS (mg/l)		AVG. O&G (mg/l)	
RUN NO.	pH	TEMP °C	RATE l/min/m^2	(GPM/ft^2)	INF	EFF	INF	EFF
1	12.0	36	254.4	(6.25)	58	7	—	—
2	12.0	39	154.7	(3.8)	58	5	—	—
3	10.2	35	162.8	(4.0)	53	18	—	—
4	9.5	52	162.8	(4.0)	42	13	53	50
5	11.1	—	162.8	(4.0)	62	16	40	28

Note: Runs 1 and 2 were declining rate; subsequent runs were manually controlled at the specified rate.

The failure of the filter to reduce oil and grease to 20 mg/l prompted an investigation of the nature of the oil and grease in the LST effluent. Duplicate samples were taken periodically over a two-week interval. One sample was analyzed for total freon extractables while the other was passed through a 0.45 micron filter and analyzed for the soluble fraction. The average total oil and grease for these samples was 35 mg/l and the soluble fraction was 31 mg/l confirming that the bulk of the oil in the LST effluent is soluble. The solubility of the oil, therefore, makes the pretreatment target of 20 mg/l unattainable by conventional technology.

Using historical operating data, a material balance was performed to assess the fate and effects of oil and grease on the activated sludge system. The 18-month data base consisted of freon extractable values obtained on a daily basis. Figure 2 illustrates the frequency distribution of the operating data. The 50-percentile values for influent and effluent oil and grease are 25 and 2.6 mg/l respectively. Soxhlet extractions of the mixed liquor indicated an average oil and grease accumulation of less than one percent of the total mixed liquor on a dry weight basis. This low level of accumulation indicates that the bulk of the freon extractables removed from the waste water were biodegraded. Since the influent oil and grease is degradable higher concentrations will not adversely effect settling properties and interfere with long-SRT operation.

Figure 2



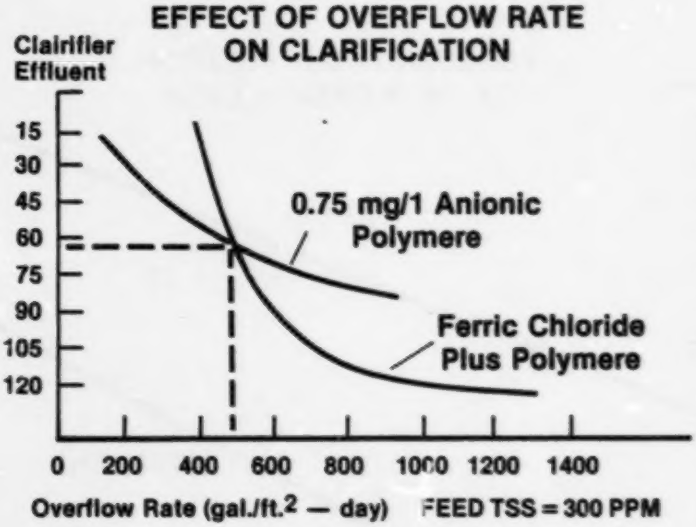
Suspended Solids Removal

The Clairton waste water is treated with lime to raise the pH prior to the fixed-ammonia still. With the high pH and excess calcium present, large amounts of calcium carbonate are precipitated. This precipitate is removed in the LST which serves to both clarify the feed to the activated sludge system and thicken the resultant inorganic sludge.

In establishing an influent solids target for a biological process, the major concerns are the nature of the solids, and their resulting impact on the biological system. Inert solids, such as the inorganic precipitate in the Clairton feed, constitute a material load which must be transported, but does not contribute to process performance. Based on experience with long SRT operation in the petroleum industry, an arbitrary pretreatment target of 20 mg/l was selected.

The results of jar tests to optimize suspended solids removal were similar to the oil and grease results which indicated that the present operational conditions were equal to or better than the alternatives. From the many alternatives evaluated, three were selected for clarification tests. Class II settling analyses were conducted to evaluate the theoretical clarification for: (1) no coagulant addition, (2) the current polymer addition scheme, and (3) a metallic coagulant with a polymeric coagulant aid. Figure 3 illustrates the relationship between overflow rate and solids removal for these three cases.

Figure 3



The tests cannot be directly compared because they were based on different samples. They are indicative, however, of the sensitivity of performance to overflow rate. The test with no coagulant addition proved to be the least sensitive to overflow rate. this sample, it should be noted, had the highest initial solids concentration, and high-solids samples seemed to clarify better throughout the testing. The metallic coagulant provided the highest overflow rate which would meet the pretreatment target of 20 mg/l suspended solids (see Table 3), but proved to be the most sensitive to changes in overflow rate. This alternative also generated larger quantities of a gelatinous, difficult-to-dewater sludge.

Table 3

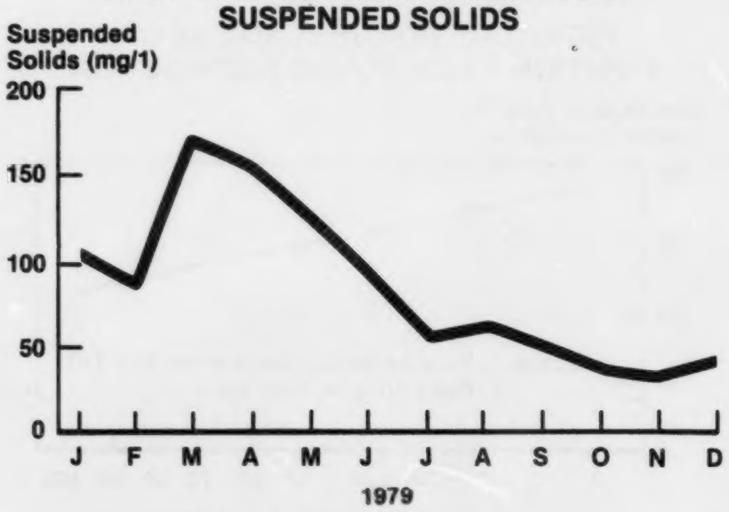
OVERFLOW RATES REQUIRED TO MEET TARGET

Test No.	Initial TSS (mg/1)	Required Removal (%)	Overflow Rate l/min/m^2	(gal/ft^2, day)
1	492	96	8,954	(220)
2	298	93	6,309	(155)
3	366	95	16,077	(395)

In all three cases, the required overflow rates are substantially less than the normal operating rate of 23,199 l/min/m^2 (570 gal/ft^2 day) for the existing clarifier. This does not imply that the LST was improperly designed, only that the high removal percentages needed to meet the pretreatment target of 20 would require extremely low overflow rates. If the target were raised to 40 mg/l, the existing overflow rate would be adequate. This is illustrated by Figure 4 which shows average effluents of 37 and 39 mg/l during the near-optimum operation which prevailed during October and November of 1979.

Figure 4

MONTHLY AVERAGE LST-EFFLUENT SUSPENDED SOLIDS



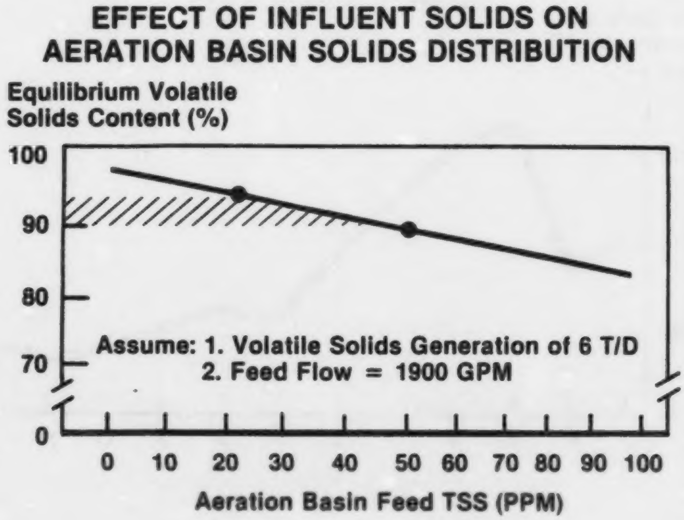
The jar-test program and settling tests indicated that the existing operational scheme of the full-scale pretreatment system was achieving near-optimum results for a gravitational-sedimentation unit. The resulting effluent quality, however, was still short of the target of 20 mg/l. Supplemental filtration was then evaluated as a means of attaining the target. The results of granular media filtration tests (Table 2) indicated that this additional process would produce an effluent quality within the preset target. Although filtration appears to be a feasible technique for attaining the desired effluent solids concentration, the validity of this target must be considered in light of full-scale operating experience.

REASSESSMENT OF PRETREATMENT TARGETS

The establishment of pretreatment targets must consider the nature of the material to be removed. In the Clairton case, the oil and grease was found to be biodegradable with no physical effects on the biomass. The only effect of these materials on the activated sludge process is the oxygen demand exerted during metabolism. Since the average influent concentration is only 26 mg/l or 283 Kg/day (624 lbs.), the impact on system oxygen resources is minor when compared to that of other contaminants. Therefore, the original oil and grease target of 20 mg/l is not applicable in this instance.

The relative impact of influent total suspended solids must be considered in light of volatile solids generation taking place within the biological system. In the case of the Clairton system, solids generation is relatively large. Typically, 5443-7257 kg (6-8 tons) of biological sludge are generated daily. Assuming that precipitation is not a contributing factor and further assuming that all external inputs have been identified, the effect of influent TSS on equilibrium levels of mixed liquor volatile suspended solids (MLVSS) can be readily calculated. Figure 5 illustrates the projected impact on the Clairton system. It is apparent that little improvement in % MLVSS is to be realized in modifying the existing system to further reduce influent TSS from the present value of approximately 50 mg/l to the previously projected target value of 20 mg/l. Thus although achieving an extemely low level of influent TSS is possible using conventional technology, in this case its incorporation would certainly not be warranted.

Figure 5



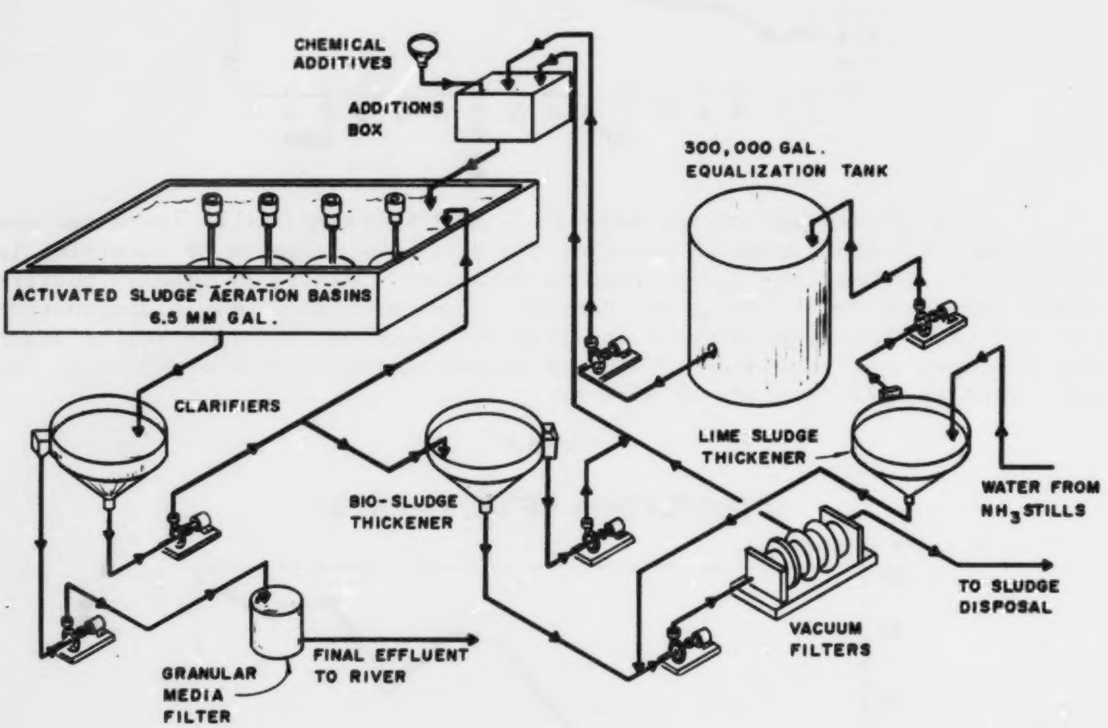
IN-PLANT VERIFICATION

In-plant investigations were initiated when the volatile solids content of the mixed liquor was less than 45 percent. Constraints imposed by the mixing capability of the aerators and the low percentage of volatile solids limited the equilibrium biological population as well as the equilibrium solids retention time. Figure 6 illustrates the Clairton biological system and its related auxiliaries. With the system equilibrated to a feed TSS content of 50 PPM, the calculated MLVSS content of 90% (see Figure 5) was considerably different than the observed value of 45%. Obviously, a source of non-volatile solids in addition to that entering with the feed water existed within the system. A careful review of operating conditions revealed the sludge wasting system to be the source of the problem.

Figure 6

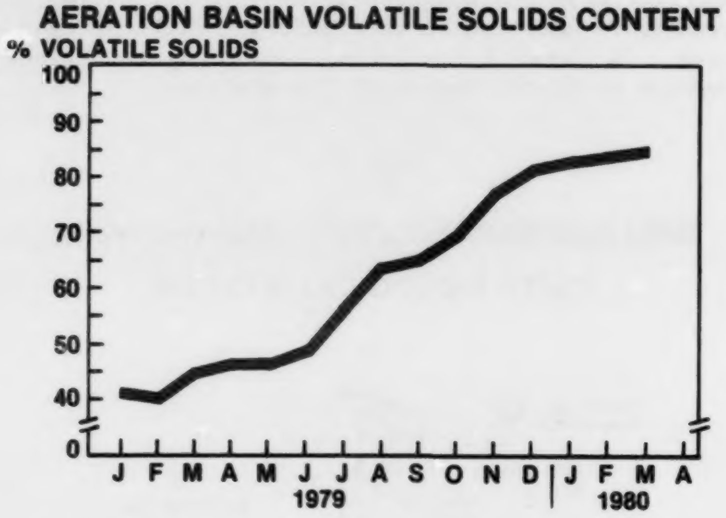
United States Steel Corporation - Clairton Works

CWTP BIOLOGICAL SYSTEM



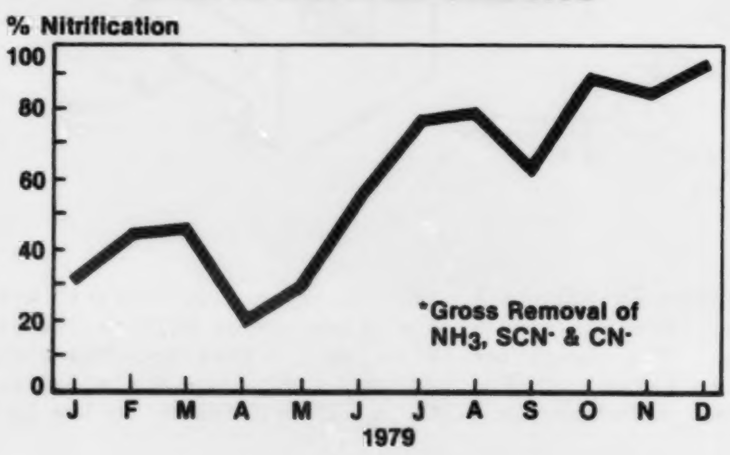
As shown in Figure 6, the rotary vacuum filters (RVF) are used to dewater sludge from the lime sludge thickener as well as bio-sludge from the aeration basins. The piping for returning filtrate from the RVF system to the aeration basins established a pathway for nonvolatile solids to enter the aeration basins. Although the filtrate is expected to be low in TSS, this did not prove to be the case. Solids which were deposited in the RVF cloth, but which were not removed from the cloth into the wastage bin were subsequently washed from the cloth and returned to the aeration basin. Although the % MLVSS was shown to be relatively insensitive to influent solids (Figure 5), the correction of the internal solids-recycle loop described above had a pronounced effect as illustrated in Figure 7.

Figure 7



The resulting improvement in % MLVSS dramatically increased the total quantity of biological material the system was capable of retaining in suspension. During the time frame in question, a series of process modifications were made to the treatment system. These modifications in conjunction with the improved climate resulting from the increased volatile solids fraction produced a significant change in system performance as typified by the improvement in nitrification (Figure 8).

Figure 8



SUMMARY

Although the prescribed limits of neither TSS nor O/G were met, the system was able to provide nitrification in a single stage system. Is is concluded that the importance of pretreatment in terms of TSS and O/G removal must be considered on an individual basis for each application. The nature and composition of so-called "oil/grease" must be determined before speculating as to its impact. Similarly, the relative quantity of daily sludge generation must be considered before establishing what would be termed "acceptable" limits on influent total suspended solids. Based upon our experience at Clairton Works, it is concluded that reasonable operation of conventional pretreatment equipment yields an influent of sufficient quality to permit maintenance of an optimum biological system.

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PROCESS CONTROL FOR ACTIVATED SLUDGE TREATMENT OF COKE PLANT WASTEWATERS

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ABSTRACT

Once an activated sludge system has been started up and brought to steady operation, control methodology must be applied to it to maintain it in such a state. Additionally, during the life of the system the situation may change from that of the original design, and the control methodology must be capable of maintaining control in such situations. This paper presents a straightforward, rapidly interpretable control methodology based on solids retention time (SRT); a methodology for determining capacities of an existing system; and, an illustration of these for a coke plant activated sludge system.

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PROCESS CONTROL FOR ACTIVATED SLUDGE TREATMENT OF COKE PLANT WASTEWATERS

INTRODUCTION

Once an activated sludge system has been started up and it has progressed to a controllable system, control methodology must be applied to maintain it in such a state. A process control methodology will be described here that is used at Koppers' facilities. This methodology is not complex and provides a base to evaluate the operational state of the system.

PROCESS CONTROL METHODOLOGY

Table 1 is a step-by-step list detailing the control procedure. This procedure is based on the use of solids retention time (SRT) as the primary independent control variable. The solids retention time (SRT) is the average amount of time suspended solids are retained in the system, and it has been shown to be a rational, convenient parameter for activated sludge design and operation.[1,2] Only the following measurements are required: aeration tank mixed liquor suspended solids (MLTSS and MLVSS), setting tank effluent total suspended solids (TSS_e), and recycle sludge total suspended solids (TSS_r). With these measured data, the effluent discharge rate, and the aeration tank volume, the rate of sludge wasting can be computed to maintain a desired SRT. A normal operating procedure would be to make these computations daily and adjust the sludge wasting rate accordingly at daily intervals. In many cases, it is possible to make the adjustment on five days per week, i.e., Monday through Friday, and leave the sludge wasting rate constant at the fifth day's setting for the remaining two days, i.e., Saturday and Sunday.

The procedure also includes a step for estimating the required rate of phosphorus addition. This step is based on the principle of adding

ACTIVATED SLUDGE PROCESS

SRT CONTROL

TABLE 1

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1. Select the desired SRT based on operational experience. Usually 20 days is reasonable for BOD, TSS, phenol, oil & grease, and sulfide removal at temperatures ranging from 15 to 20°C.

2. Calculate the weight of total suspended solids (TSS) in the aeration tank daily as:

   M in lbs = (MLTSS) (V) (8.34)

   where MLTSS = aeration tank total suspended solids concentration as measured, mg/l; V = aeration tank volume, million gallons; and, 8.34 = conversion factor, mg/l to lb/million gallons.

3. Determine the total weight of TSS to be wasted daily as:

   $$\text{lbs to waste per day} = \frac{M}{SRT}$$

4. Calculate the total weight of TSS lost daily in the clarifier overflow as:

   $$\text{L in lbs lost per day} = (Q)\ (TSS_e)\ (8.34)$$

   where Q = effluent TSS as measured, mg/l (composite sample if possible).

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continued

5. Determine the weight of TSS to be intentionally wasted daily as:

$$\text{PI in lbs to intentionally waste per day} = \frac{M}{SRT} - L$$

6. Determine the volume of recycle sludge to be drawn off daily to achieve this intentional wasting of TSS as:

$$\text{w in million gallons} = \frac{PI}{(TSS_r)(8.34)}$$

where TSS_r = recycle sludge TSS concentration as measured, mg/l.

7. Determine the phosphoric acid addition rate based on the production of volatile suspended solids (MLVSS) as:

$$\text{Phosphoric Addition Rate in Gallons per Day (gpd)} = \frac{(MLVSS)(V)(8.34)(P{:}MLVSS\ Ratio)}{(P\ Content\ of\ H_3PO_4)}$$

where, MLVSS = VSS of aeration tank as measured, mg/l; $\frac{P}{MLVSS}$

= ratio phosphorus content of VSS, usually 0.024 is reasonable; and, P content of phosphoric acid = as specified, e.g., for 75% H_3PO_4 the P content is 3.13 lb P/gallon.

the phosphorus removed by biomass losses from the system. The biomass is estimated by the volatile suspended solids (VSS) concentration. The VSS removal from the system can be estimated, and then based on the phosphorus content of the VSS and the phosphoric acid, the required amount of phosphoric acid addition can be computed. A value of 0.024 lb P/lb VSS is suggested for the phosphorus content of the VSS. However, this ratio can be different depending on the system, and it should be adjusted as necessary based on operating experiences. The soluble effluent phosphorus should be monitored to provide a basis for adjusting this computation.

Table 2 is a recommended daily data sheet that facilitates this control methodology. A data sheet similar to this one was originally proposed for use with municipal activated sludge systems.[3]

CAPACITY ESTIMATION

Once an activated sludge system has been brought into steady operation, it is desirable to adjust it to an optimal operation for the specific situation. The operating situation will often be different from that of the original design and may change during the life of the system. Wastewater flow rates and compositions will vary with production rates and process changes.

For an existing system the solids retention time (SRT) and recycle ratio (r) are usually the only adjustable parameters. The hydraulic retention time (HRT) is fixed by the feed rate of wastewater to be treated and can be adjusted for process control only if there are multiple aeration basins available. The day-to-day variation in HRT due to flow variation is considered not to be part of the process control in this discussion.

As stated in Table 1, a 20 day SRT is normally satisfactory for phenol, BOD, TSS, oil & grease, and sulfide removal at temperatures ranging from 15 to 20°C. However, there may be cases where both higher or

ACTIVATED SLUDGE PROCESS

SRT CONTROL

TABLE 2

Operator ______________________________ Date ______________________________

Aeration Tank Volume

V = __________ million gallons

1. Operational SRT __________ days

2. Mass TSS in aeration tank (M):

   MLTSS = __________ mg/l

   M = (MLTSS(V)(8.34)

   M = __________ lbs

3. Mass TSS that must be removed in M ÷ SRT __________ lbs/day

4. Mass TSS lost in settling tank effluent (L):

   Effluent TSS = __________ mg/l

   L = (Q)(Effluent TSS)(8.34)

   L = ____________ lbs/day

Effluent Daily Discharge

Q = __________ million gallons per day

5. Mass TSS to intentionally waste (PI):

   PI = (M ÷ SRT) - L

   PI = ____________ lbs/day

6. Waste sludge flow rate (from recycle sludge lines)(w):

   Recycle Sludge TSS (TSS_r) __________ mg/l

$$w = \frac{PI}{(TSS_r)(8.34)} \times 1,000,000$$

   w = ______________ gpd

$\frac{P}{MLVSS}$ Ratio = __________

P Content of Phosphoric Acid = ____________ lbs/gal

7. Phosphoric acid addition required:

   MLVSS = ______________ mg/l

   MLVSS Production = (MLVSS)(V)(8.34) ÷ SRT

   MLVSS Production = ______________ lbs/day

   lb P required = (MLVSS Production) ($\frac{P}{MLVSS}$ Ratio)

   lb P required = ________________ lb/day

   Phosphoric Acid addition rate = (lb P required) ÷ (P content)

   Phosphoric Acid addition rate = ______________ gpd

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in operation, it is ususally best to operate at as high an SRT as system capacity permits. At higher SRT values sludge production and hence, sludge wasting and disposal, are less. Thus, any costs associated with sludge disposal are reduced.

In addition to reduced sludge production, operation at longer SRT values maintains a higher biomass in the system. The higher biomass provides greater stability to transient conditions because there is more biomass to respond to loading increases. Figure 1 is a graph showing the relationship of MLTSS, MLFSS, and MLVSS concentrations to SRT for an operation system. The appropriate equations are shown on the graph. Equations used in this paper have been presented elsewhere and, they are not commented on in detail here.[1,4,5] The trend of higher concentrations at longer SRT values is illustrated by this graph. Finally, effluent quality due to biological oxidation improves with increasing SRT. In particular, soluble phenol and BOD concentrations would decrease at longer operating SRT values.

Two factors will limit the maximum SRT value that can be achieved by an operatng system for a given wastewater loading: 1) settling tank capacity; and, 2) aerator capacity.

The activated sludge settling characteristics must be known to evaluate the settling tank capacity. These characteristics are determined by performing zone settling tests on the activated sludge after steady system operation has been achieved. An illustrative example will be provided here based on experiences at Koppers facilities.

Figure 2 shows the zone settling velocity (ZSV) of activated sludge at two Koppers facilities as a function of its TSS concentration as measured by zone settling tests. Plant A is a by-product coke plant producing foundry coke at the time of settling tests. Wastewater pretreatment included ammonia removal from the excess flushing liquor using a lime still and equalization in a feed tank. Plant B is a coal tar distillation plant.

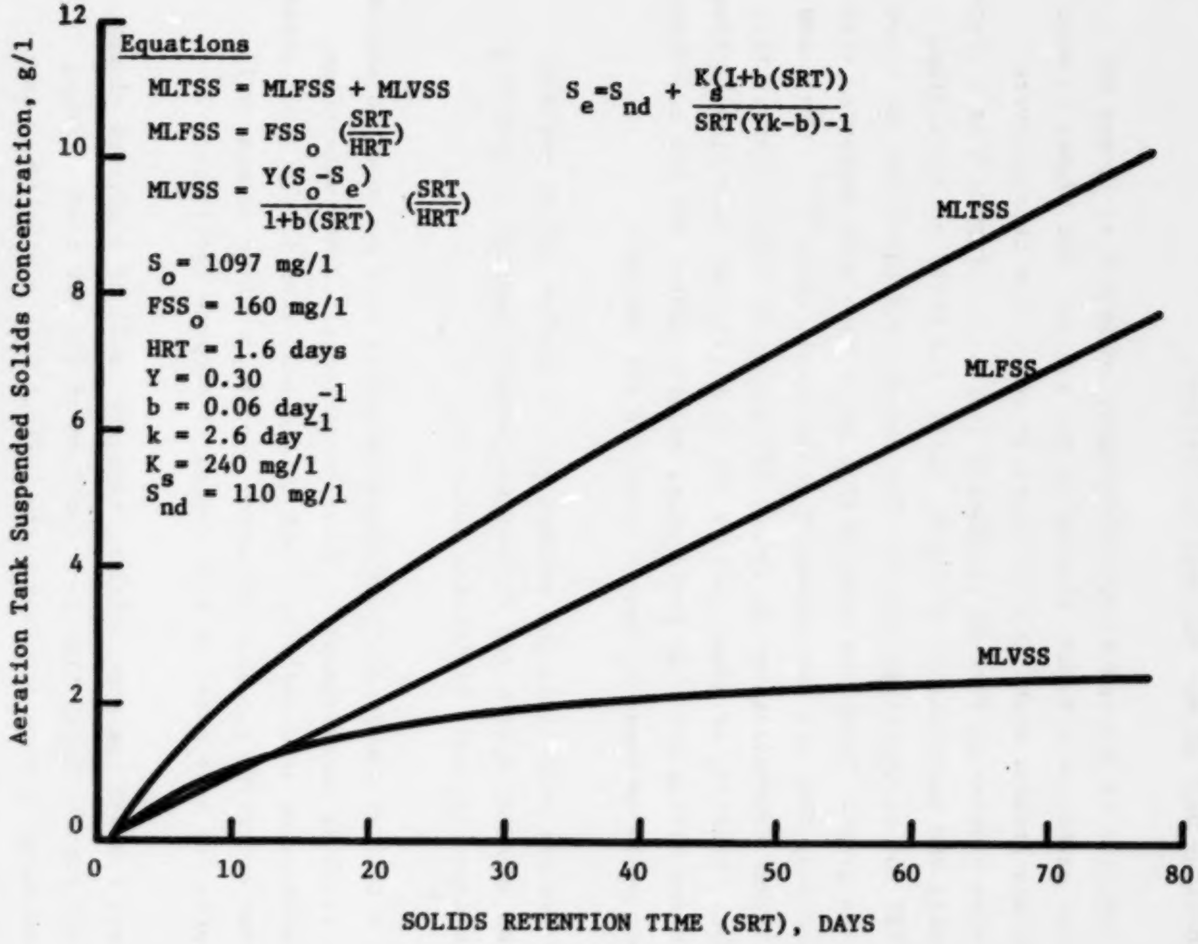

Figure 1. Relationship of MLTSS, MLFSS, and MLVSS To Solids Retention Time.

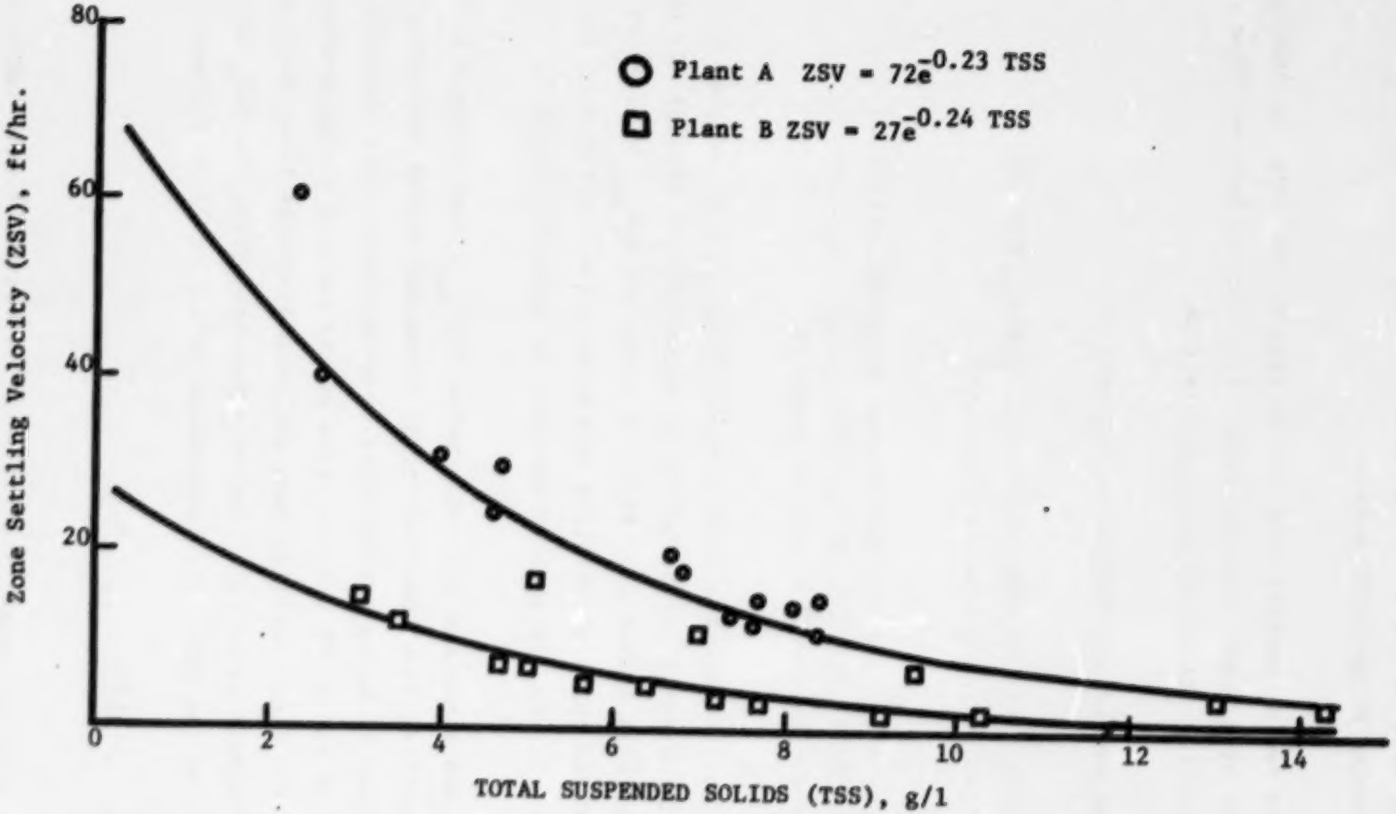

Figure 2. Relationship of Activated Sludge Zone Settling Velocity To Total Suspended Solids Concentrations.

The settling characteristics are described by the equations shown on the graph. The ZSV decreases exponentially as the TSS increases. The difference in the settling characteristics is probably due to the differing MLVSS/MLTSS ratios.

There are two parameters that can be used to evaluate the loading condition of a final settling tank: (1) the surface overflow rate (SOR), and (2) the solids loading rate (SLR).

These parameters are defined as follows:

$$\text{SOR} = \frac{\text{final settling tank effluent discharge rate, gpd}}{\text{effective upflow surface area,ft}^2} \qquad (1)$$

$$\text{SLR} = \frac{\text{mass flow rate of mixed liquor suspended solids to the final settled tank, lb/day}}{\text{effective downflow surface area, ft}^2} \qquad (2)$$

The SOR has a maximum allowable value (SOR_{max}) that depends on the mixed liquor total suspended solids concentration (MLTSS) and the settling characteristics. Figure 3 shows the SOR_{max} as a function of the MLTSS based on settling characteristics described by the equations in Figure 2. The appropriate equation is shown on Figure 3.

The SLR has a maximum allowable value (SLR_{max}) that depends on the final settling tank underflow total suspended solids concentration (TSS_r) that is being attempted to be maintained. This concentration depends on the MLTSS and the ratio of the recycle sludge pumping rate to the final settling tank effluent discharge rate; this ratio is the recycle ratio (r). The equation describing the TSS_r as a function of the MLTSS and independent variables is as follows:

$$\text{TSS}_r = \frac{\text{MLTSS}}{r}\left(1+r - \frac{\text{HRT}}{\text{SRT}}\right) \qquad (3)$$

In many specific cases, the ratio HRT/SRT is relatively small compared to the (1+r) term, and it can be neglected without sacrifice of signif-

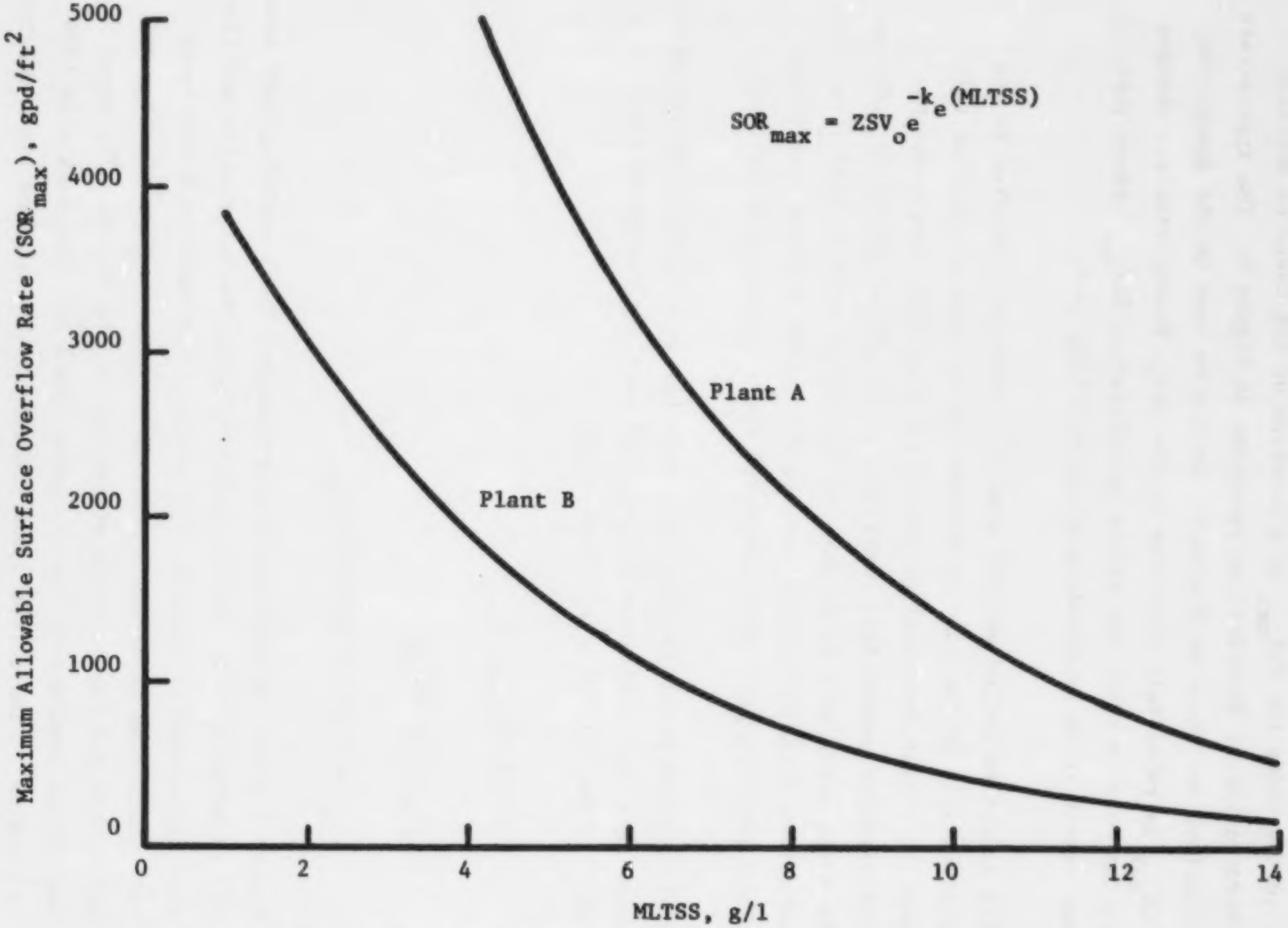

Figure 3. Relationship of Maximum Allowable Surface Overflow Rate To MLTSS.

icant accuracy. The resulting equation is then as follows:

$$TSS_r \simeq \frac{MLTSS}{r}(1+r) \tag{4}$$

Figure 4 shows the SLR_{max} as a function of TSS based on settling characteristics described by equations in Figure 2. The appropriate equations are shown on Figure 4. As can be seen in the graph, the SLR_{max} is relatively sensitive to the TSS_r. Hence, reckless changes in the recycle ratio can result in unexpected SLR_{max} values that may result in an overloading of the settling tank.

The effective upflow surface area of a circular clarifier is the surface area of the annulus between the peripheral overflow weir and the center feed well corrected for non-ideal flow patterns. For circular center feed clarifiers a correction factor of 0.55 can be used, i.e., only 55 percent of the actual area is effective. The effective downflow surface area is the entire surface area of the final settling tank again corrected for non-ideal flow patterns.

The required final settling tank area (A) is a function of the MLTSS, flow rate (Q), recycle ratio (r), and settling characteristics (k_e, ZSV_o). The following equations apply:

$$A = \max(A_{clar}, A_{zsr}) \tag{5}$$

$$A_{clar} = Q/SOR_{max} \tag{6}$$

$$A_{zsr} = (1+r)(Q)(MLTSS)/SLR_{max} \tag{7}$$

Figure 5 shows the relationship of required final settling tank area (A) to MLTSS and recycle ratio for settling characteristics and flow rate applicable to Plant A. In general, the value of A increases with increasing MLTSS and decreasing r. The portions of the graph not within the capabilities of the system are shaded. The upper horizontal boundary is the available final settling tank area (950 ft^2 upflow). The curved lower boundary is the minimum area required

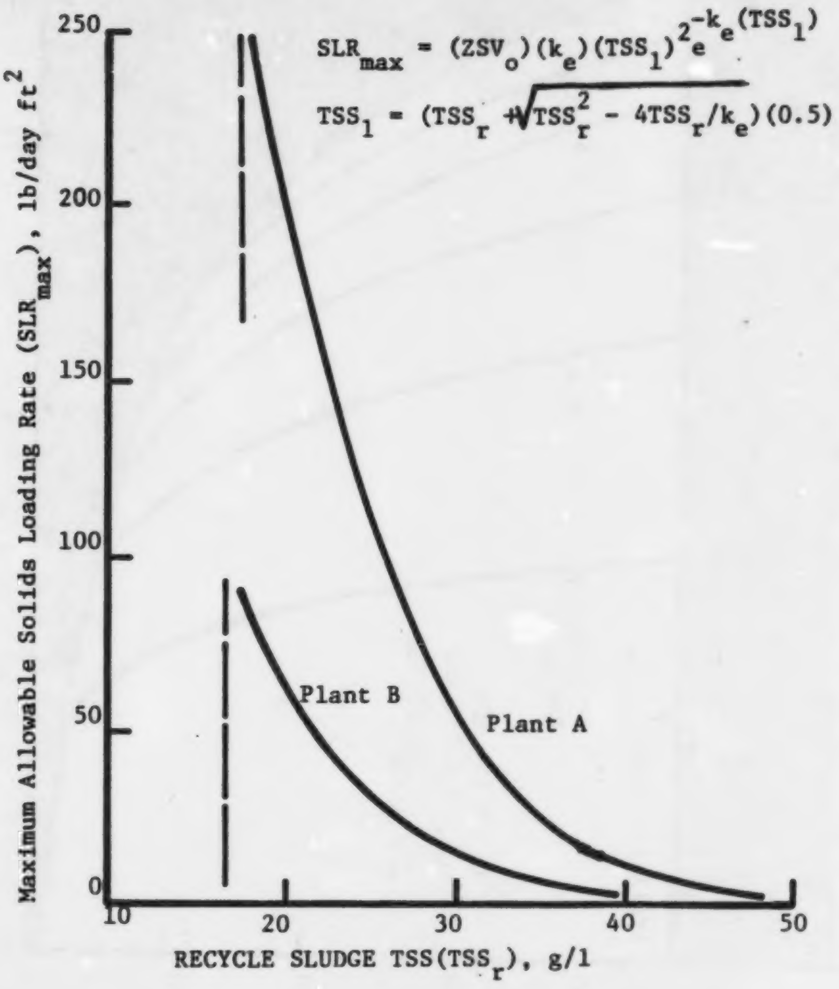

Figure 4. Relationship of Maximum Allowable Solids Loading Rate to Recycle Sludge TSS.

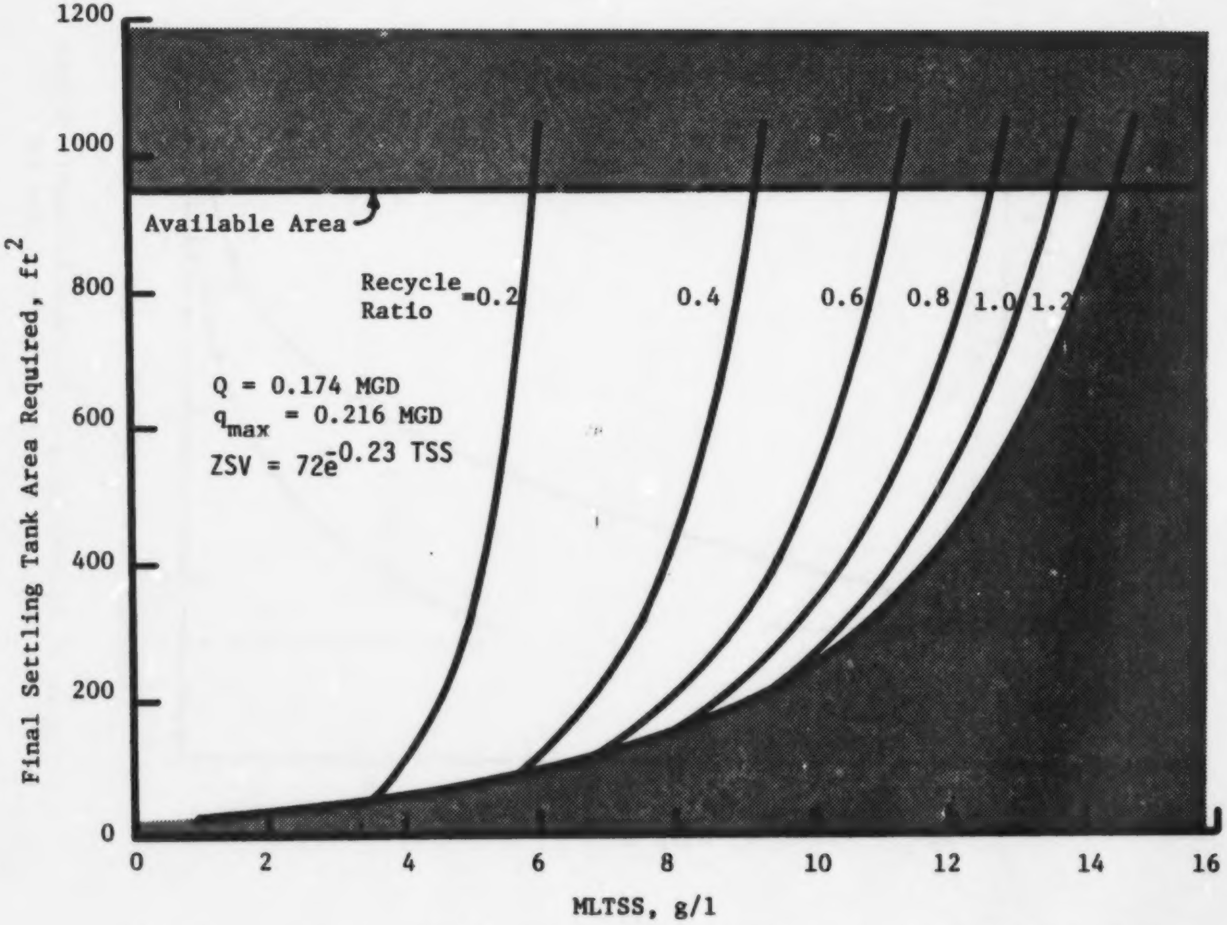

Figure 5. Relationship of Required Final Settling Tank Area to MLTSS and Recycle Ratio (r).

at the maximum recycle ratio (1.24; the recycle sludge pump is sized for 150 gpm). Any combination of MLTSS and r not lying in the shaded portions is within the system's capabilities. The value of r would be adjusted by changing the flow rate of the recycle sludge pump; the value of the MLTSS would be adjusted by changing the SRT as required according to Figure 1.

The oxygen uptake rate varies with the SRT value because the degree of biological oxidation of influent pollutants and the microbial respiration are dependent on SRT. Hence, for an activated sludge system with fixed aeration capacity, the aeration tank dissolved oxygen (DO) concentration will vary with SRT. Figure 6 shows this variation for Plant A and the conditions listed. The aeration tank DO decreases with increasing SRT. The decrease is relatively sharp at SRT values less than 10 days, and more gradual at higher values. At SRT values less than 10 days for this situation, the degree of oxidation increases greatly with increasing SRT giving a sharp increase in oxygen consumption and thereby the sharp decrease in aeration tank DO. At higher SRT values the increase in oxygen uptake is more dependent on microbial respiration which increases with increasing bacterial mass as shown in Figure 1.

Normally, for coke plant wastewaters a minimum aeration tank DO of 2.0 mg/l is recommended to sustain consistent, reliable phenol and BOD_5 removal. A vertical boundary is shown on Figure 6 at the SRT value where the aeration tank DO equals 20 mg/l. The region of the graph to the right is shaded as being beyond the recommended limits of the system. Hence, a constraint is placed on the allowable operational range of the SRT in addition to those due to settling characteristics.

EXAMPLE

A series of graphs have been presented showing various parametric relationships for an existing activated sludge system (Plant A). This system was designed to operate at a 20 day SRT and a recycle ratio of 1.0. For a hydraulic retention time (HRT) of 1.6 days,

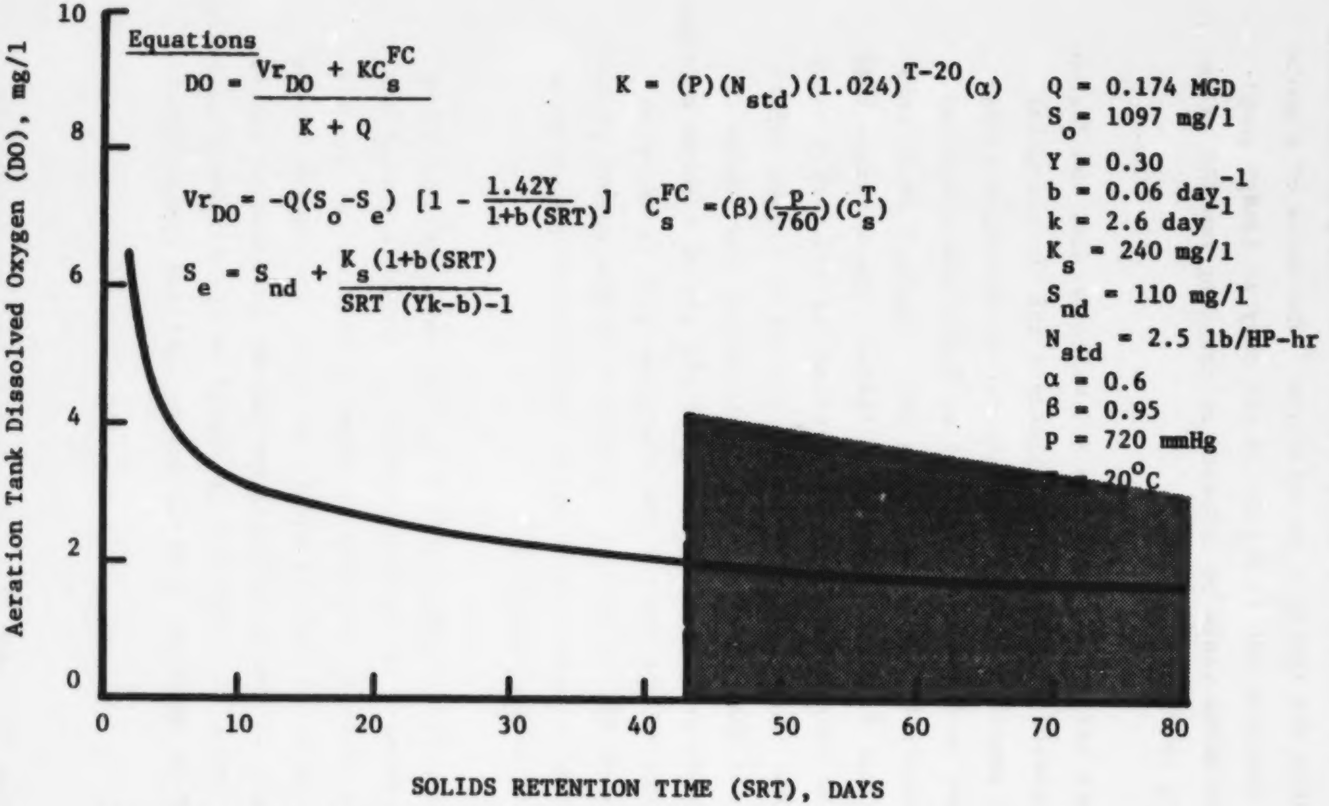

Figure 6. Relationship of Aeration Tank Dissolved Oxygen Concentration to Solids Retention Time.

an influent COD (S_o) of 1097 mg/l, an influent FSS (FSS_o) of 160 mg/l, and a flow (Q) of 174,000 gpd, the graphs indicate the system to be operating well within its capabilities. Figure 1 gives a MLTSS of approximately 3600 mg/l for an SRT of 20 days. Figure 5 gives a required settling tank area of approximately 60 ft^2 for a MLTSS of 3600 mg/l and a recycle ratio of 1.0. Figure 6 gives an aeration tank DO of approximately 2.6 mg/l for an SRT of 20 days.

The available settling tank area is in excess of that required. The difference is due to the measured full-scale settling characteristics being superior than those used for original design. The difference is apparently due to a large amount of inert fines flocculated with the sludge at the time of the settling tests. These fines increased the specific gravity of the floc particles and hence, the settling velocity.

Given this series of graphs, the following questions could be posed:

1. What is the maximum SRT and minimum recycle ratio that this system could be expected to be operated at?

2. What would be the advantages of making such changes?

To begin with, determine the maximum SRT allowable due to aeration constraints. On Figure 6, this value is approximately 43 days to maintain an aeration tank DO of 2.0 mg/l. Use a value of 40 days so that some excess remains. On Figure 1, an SRT value of 40 days results in a MLTSS value of approximately 6100 mg/l. On Figure 5, a MLTSS value of 6100 mg/l gives a required settling tank area of 950 ft^2 at a recycle ratio of slightly greater than 0.20. Use a value of 0.30 so that some excess remains. Hence, it would not be unreasonable to attempt a state with an SRT of 40 days and a recycle ratio of 0.30. It would be recommended that operational changes to go from an SRT 20 days to 40 days and a recycle ratio of 1.0 to 0.30 be done in stages, i.e., to 30 days and 0.6 for several weeks, then to 40 days and 0.3.

After each change of state is made, the system should be observed for deleterious effects at the new state. The graphs are approximations of reality, and unexpected effects can occur. The following are some possible effects that may not be accounted for in the graphs:

1. Some nitrification may occur at the longer SRT values resulting in increased oxygen uptake rates and a more rapid decrease in aeration tank DO values. Significant nitrification has not normally been observed to occur in undiluted coke plant wastewaters at SRT values less than 50 days without the use of activated carbon addition to the aeration tank.

2. Reducing the recyle ratio increases the residence time of the recycle sludge in the final settling tank. If some nitrification occurs, the longer residence time may allow reduction of nitrate to nitrogen gas (denitrification) within the sludge causing it to float to the surface of the settling tank.

3. An overloaded condition for the aerator or settling tank can occur before it is expected because the graphs may not be as precise as expected.

If any of the above effects are observed, the correctional procedure is to reverse the direction of the change until the effect disappears. It should also be noted that the change of state could go beyond what is predicted by the graphs. If there were no deleterious effects at a 40 day SRT and a recycle ratio of 0.30, it would be recommended that the SRT be increased and the recycle ratio be decreased further in smaller increments until such effects were observed.

At the longer SRT values, the following changes would be expected:

1. improved soluble effluent quality, i.e., lower phenol and soluble BOD_5 concentrations.

2. decreased sludge mass production.

3. decreased phosphoric acid additions.

At the lower recycle ratio values, an increased recycle sludge TSS (TSS_r) would be achieved. An increased TSS_r would result in a decreased waste sludge volume flow rate.

The improved effluent quality is difficult to quantify, because of the lack of detailed biokinetic studies on coke plant wastewater. An example of the possible improvement at these SRT values might be a reduction in average effluent phenol concentration from 0.9 ppm to 0.6 ppm or thereabouts.

The decreased sludge production can be estimated using the SRT control procedure outlined in Tables 1 and 2. Assuming no loss of solids in the effluent for this computation and using SRT values of 20 and 40 days, MLTSS values of 3600 and 6100 mg/l, an aeration tank volume of 0.278 mil gal in Steps 1,2,3,4,5 of Table 2, sludge production rates can be estimated. The results are 417 lb/day and 353 lb/day for the 20 and 40 day SRT values, respectively. Using Equation 3, the recycle sludge TSS concentrations can be estimated. The results are 6912 mg/l and 25,620 mg/l for a 20 day SRT, 1.0 recycle ratio and a 40 day SRT, 0.3 recycle ratio, respectively. The waste sludge flow rates can be estimated using Step 6, Table 2. The results are 7233 gpd and 1652 gpd for the two above states, respectively. The phosphoric acid addition rates can be estimated using MLVSS values from Figure 1 in Step 7, Table 2. The results are 1.42 gpd and 0.93 gpd for the two above states, respectively.

CONCLUSION

A straightforward, rapidly interpretable control methodology has been presented. The methodology makes possible the rapid identification and control of the state of operation of an activated sludge sytem, i.e., the SRT, HRT, and r value. Procedures have been presented to estimate the capacity of an existing system for a specific situation. The procedures make possible rational changes in the state of a system, to approach an optimal operational state.

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NOTATION

A - final settling tank surface area, L^2

b - decay coefficient, T^{-1}

C_s^{FC} - saturation DO at field conditions, M/L^3

C_s^{20} - saturation DO at 20°C, M/L^3

TSS_r - total suspended solids concentration of final settling tank underflow, M/L^3

V - aeration tank volume, L^3

α - oxygen transfer coefficient

β - DO saturation coefficient

DO - dissolved oxygen concentration, M/L^3

FSS_o - influent fixed suspended solids concentration, M/L^3

k - maximum specific COD utilization rate, T^{-1}

k_e - empirical settling coefficient, L^3/M

K_s - Monod coefficient, M/L^3

MLFSS - mixed liquor fixed suspended solids concentration, M/L^3

MLTSS - mixed liquor total suspended solids concentration, M/L^3

MLVSS - mixed liquor volatile suspended solids concentration, M/L^3

N_{std} - standard aerator oxygen transfer capacity, lb O_2/HP-hr

P - aerator power

p - atmospheric pressure, mm Hg

Q - influent flow rate L^3/T

q - recycle sludge pumping rate, L^3/T

r - recycle ration (q/Q)

r_{DO} - volumetric oxygen uptake rate, M/L^3-T

S_e - effluent COD concentration, M/L^3

S_o - influent COD concentration, M/L^3

T - temperature, °C

BIOLOGICAL TREATMENT OF COKE PLANT WASTE USING AN INTEGRAL CLARIFICATION CONCEPT

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Introduction

Armco's Hamilton plant is located in New Miami, Ohio, on the Great Miami River. The plant produces molten pig iron, metallurgical coke, coke gas, and coking by-products.

The Hamilton Coke Plant consists of four Koppers-Becker underjet design batteries with a total of 110 ovens. The oldest battery was constructed in 1928 and the newest started up in 1947. During this period the batteries have been rebuilt several times.

In 1976, Armco initiated an extensive modification and rehabilitation program for all four coke batteries. A major part of this program was the installation of state-of-the-art air and water pollution control facilities. The water pollution control program included the collection and treatment of sanitary sewage, ammonia still waste, benzol plant waste, quench tower waste, and high temperature noncontact cooling water. This paper specifically deals with the treatment of the sanitary sewage, ammonia still waste, and the benzol plant waste.

Background

The wastewaters generated at Armco's Hamilton Coke Plant are primarily from the flushing liquor system and the benzol plant. The flushing liquor is hot water which is sprayed directly into the collecting mains to quench coke oven gas as it leaves the ovens. A circulating liquor system is used to cool the gas in direct spray primary coolers. Water evaporated from the coal is condensed in the main and primary coolers creating excess flushing liquor. This highly contaminated excess liquor from the two systems is collected in storage tanks prior to treatment.

Several sources of wastewater from the benzol plant are collected in a common oil separation sump. The largest source is condensate from wash oil/crude light oil distillation operations. The wash oil is purified by steam stripping to remove crude light oil that was absorbed in the light oil gas scrubbers. The steam condensate is discharged to the benzol sump as a contaminated waste stream. See Table I for the design volumes and chemical composition of the raw excess ammonia liquor and benzol plant wastewater.

At the outset of the program, a study was conducted to determine the best approach for treating coke plant wastewater. Alternatives studied and

TABLE I

RAW WASTE WATER - DESIGN COMPOSITION

	Excess Ammonia Liquor			Benzol Plant Waste		
	mg/l	kg/day	(#/day)	mg/l	kg/day	(#/da
AVERAGE FLOW GPD		58,300			43,100	
Ammonia-N	4625	1020	(2247)	13	2.3	(5)
Cyanide	25	5.5	(12)	19	3.2	(7)
Thiocyanate	1400	310	(680)	18	2.7	(6)
Oil & Grease	10	1.8	(4)	45	7.3	(16)
Phenol	1140	250	(550)	114	19	(41)
Sulfide	23	5	(11)	11	1.8	(4)
Suspended Solids	60	14	(30)	40	6.4	(14)
COD	8180	1820	(4000)	550	90	(200)
TOC	2350	520	(1140)	540	88	(195)
pH	9.0			7.2		

rejected included physical-chemical treatment with activated carbon and joint treatment in a publicly-owned treatment works (POTW). The physical-chemical scheme offered a lower capital investment but a much higher operating cost and was thus rejected. The joint treatment scheme was rejected because of the remote location of the coke plant and the unique configuration of the POTW. Thus, a combination of physical-chemical treatment followed by biological treatment was chosen. The major treatment objective was compliance with NPDES permit requirements. In order to meet this objective, each major waste stream had to be pretreated by physical-chemical methods to remove incompatible pollutants prior to biological treatment.

Physical-Chemical Pretreatment

The benzol plant waste contains large quantities of oil. During the original survey the majority of this oil was free or floatable oil with less than 30 mg/l of emulsified oil. However, the light oil recovery operation has since been modified, and the waste stream now contains 800 mg/l of emulsified oil. The free oil is partly removed in the existing oil separation sump. However, this sump is not capable of handling large oil spills. Because of the potential detrimental effect of large quantities of free oil on the biological treatment plant, additional oil removal equipment was installed to help contain spills. This equipment consists of a prepackaged gravity oil/water separator. The separator is installed in series with the existing sump and designed to remove free oil that passes through the primary separation tank. After treatment in this separator, the water is pumped to the biological treatment plant. To date, the emulsified oil has caused no apparent problems at the bioplant.

Excess ammonia liquor contains large quantities of ammonia, sulfide, cyanide, and other compounds which can inhibit biological oxidation(1,2). The ammonia is present in two forms, commonly referred to as "free" and "fixed" ammonia(3). Free ammonia, including ammonium hydroxide, ammonium carbonate, ammonium sulfide, ammonium cyanide, etc., is easily dissociated and removed by steam stripping. Fixed ammonia salts, including ammonium chloride, ammonium thiocyanate, ammonium sulfate, etc.(3) are dissociated and removed by raising the pH with an alkaline material and steam stripping. To enable the final effluent to meet the NPDES permit requirements a steam distillation system was installed to remove the free and fixed ammonia, cyanide, and sulfide. This system was chosen over other concepts being used in the industry because of economics and site specific factors.

The alkaline material used to dissociate the fixed ammonia at Hamilton is caustic soda. A solution of 50% sodium hydroxide is injected directly into the still without additional dilution. Caustic soda was chosen over the more traditional material, milk of lime, because of simplified operation and fewer maintenance problems. The addition of caustic requires only the installation of a storage tank and a metering pump, rather than the complex feeding system required for lime, with a resultant lower capital cost. The pH at the top of the fixed still can be controlled, thus eliminating the swings in pH at the bottom of the still due to the long lag time in the still, and the problem of fouling the still with lime has been eliminated. Another advantage, as yet not fully evaluated, is that caustic eliminates suspected problems caused by high concentrations of calcium in the bioplant feed associated with lime stills. The major disadvantage of caustic is that it costs several times as much as an equivalent amount of lime.

An ammonia still originally installed in 1954 as part of the Middletown Coke Plant and retired in 1976 was relocated to the Hamilton Coke Plant. The still contains 5 free ammonia (free leg) trays and 10 fixed ammonia (fixed leg) trays. The trays are all standard cast iron single bubble cap plate sections. The system is equipped to use 50% sodium hydroxide as the alkaline material necessary to dissociate fixed ammonia. A second "standby" ammonia still was installed for use during maintenance and cleaning of the primary still. The second still is a standard pressure vessel column with float valve type, tower filler trays. The ammonia still system includes an automatic pH monitoring and control system which measures and records the pH of the still discharge as well as controlling the amount of caustic fed to the fixed leg.

Excess ammonia liquor is injected into the free leg of the ammonia still near the top of the still column. After passing through the free leg, the liquor is removed and caustic added and mixed with a motionless mixer. The high pH liquor is then injected into the fixed leg. Low pressure exhaust steam is injected at the base of the still, which is bubbled through the descending flow of liquor to strip the ammonia. The ammonia vapors and other acid gases are collected at the top of the still, cooled to condense excess water, and discharged into the coke gas downstream of the primary cooler. The ammonia is later recovered from the gas as ammonium sulfate, a by-product. The still wastewater with little remaining ammonia is pumped to the biological treatment plant.

Design Considerations

The biological system was designed from actual wastewater flows and analysis (Table II and III), data in the literature$^{(1,4,5,6,7,8,9)}$, and information gathered while inspecting most of the operating coke plant biological treatment systems in North America. The most significant findings of this predesign investigation were: 1) the need for extended equalization, primarily to equalize the wide fluctuation in wastewater chemistry; 2) a minimum aeration detention time of 24 to 48 hours; 3) the need for completely mixed aeration to minimize the concentration of toxic parameters; 4) the possibility of achieving both carbon oxidation and nitrification in a common aeration tank; 5) the need to add phosphorus to support bio growth; 6) the universal problem with aerator foaming; and 7) the need to control pH and temperature. In addition, the investigation uncovered an innovative clarification system that might be used to great advantage in coke plant biotreatment. The system incorporates an integral clarifier with scraper mechanism to direct the settled sludge back into the aeration basin. In late 1976, there were no similar operating systems in the United States, although several were operating in Canada. In December 1976, a trip was taken to observe operating systems in Quebec$^{(10)}$ and Ontario, Canada$^{(11)}$. Following this trip, it was concluded that the concept offered several advantages, including potential capital cost savings, elimination of a separate sludge return system, potential for improved treatment, and substantial land savings. Therefore, in February 1977, the engineering firm of Burns & McDonnell was instructed to proceed with the design of the biological treatment system utilizing this integral clarifier concept with provisions to achieve nitrification and with the capability to add a second stage nitrification reactor should it be required.

In November 1977, construction commenced with the clearing of the site. The work proceeded very slowly through the winter months, and in March 1978, the first major pour of concrete was made. The work progressed through the summer of 1978 and because of many delays caused by a wet spring and summer,

TABLE II

BIOLOGICAL TREATMENT PLANT INFLUENT

	Design Composition			Actual Composition*		
	mg/l	kg/day	(#/day)	mg/l	kg/day	(#/day)
Flow:						
Ammonia Still Waste		64,600 GPD			--	
Benzol Yard Sump		43,100 GPD			--	
Misc. Waste		10,900 GPD			--	
Total Process		118,600 GPD			102,500 GPD	
Sanitary		21,800 GPD			35,100 GPD	
Total Contaminated Waste Water		140,400 GPD			137,600 GPD	
Dilution Water		73,800 GPD			61,400 GPD	
Total Plant Feed		214,200 GPD			199,000 GPD	
Ammonia-N	80	70	(150)	115	85	(190)
Cyanide	5	3.6	(8)	3	2.3	(5)
Thiocyanate	400	320	(700)	175	130	(285)
Oil & Grease	12	10	(22)	45	35	(75)
Phenol	250	200	(440)	180	135	(300)
Suspended Solids	40	32	(70)	70	55	(120)
COD	1800	1500	(3300)			
TOC	600	500	(1100)			
pH		7.0-10.0				
**Detention time - total feed		- 30 hours			32 hours	
**Detention time - process & sanitary		- 45 hours			46 hours	
Clarifier Overflow Rate-Total Feed		300 GPD/SF			275 GPD/SF	
Clarifier Overflow Rate-Process & Sanitary		200 GPD/SF			190 GPD/SF	
Clarifier Weir Loading-Total Feed		4,100 GPD/LF			3,800 GPD/LF	
Clarifier Weir Loading-Process & Sanitary		2,700 GPD/LF			2,650 GPD/LF	

*October 1979-March 1980: 6-month average of 30-day averages.
**Based on aeration tank volume (including chimney) of 265,000 gallons.

TABLE III

BIOLOGICAL TREATMENT PLANT EFFLUENT

	Design Composition			Actual Composition*		
	mg/1	kg/day	(#/Day)	mg/1	kg/day	(#/day)
Flow:	214,200 GPD			199,000 GPD		
Ammonia-N	180	145	(316)	7	6	(13)
Cyanide	4.5	3.6	(8)	1.5	1	(2.5)
Thiocyanate	-	-	-	4	3	(7)
Oil & Grease	12	10	(22)	5	4	(8)
Phenol	3.0	2.3	(5)	0.001	0.007	(0.015)
Suspended Solids	70	60	130	32	25	(55)
pH		6.0-9.0				

*October 1979 - March 1980: 6-month average of 30-day averages construction carried over into the winter of 1979. Fortunately, the winter of 1979 was relatively mild and the plant was ready to be started in March of 1979.

Description of Facilities

The treatment plant process flow schematic is shown on Figure 1. The incoming waste is received at the plant in one of two surge tanks. The process surge tank, which is 40 feet in diameter by 40 feet tall with a working capacity of 300,000 gallons, receives waste from the ammonia still system and the benzol plant. The tank provides flow and chemical equalization by operating at 50% full and using the side entering mixer shown in Figure 2. Process waste is normally stored in the surge tank for approximately one day before it is pumped to the aeration basin. The sanitary surge tank shown on Figure 3 receives the sanitary sewage generated in the coke plant area, and gas seal water from the flare stack. This tank is agitated with air to insure a non-septic waste. After equalization, the sanitary waste is combined with the process waste and discharged into the aeration basin.

The ammonia liquor from the still is approximately 105°C and must be cooled to approximately 25°C(4) for optimum ammonia removal in the bioplant. This cooling is achieved in part by flash cooling at the still and natural heat loss in the surge tank, with the final cooling achieved in two parallel spiral flow heat exchangers. To compensate for the hot blower air used in the aeration process, the liquor is cooled to around 20°C during the summer months.

In order to maintain the nutritional balance(1) of the aerobic system, phosphoric acid is added to the liquor just after the heat exchangers. At the same point, sulfuric acid is added for pH control should the basin pH exceed the desired 7.8 operating point. Following chemical addition, the total flow is discharged into two parallel aeration/clarification basins.

The treatment system utilizes a completely mixed, activated sludge extended aeration concept with an integral clarifier. The aeration portion of the plant contains two cubical concrete basins each with its own clarifier section. Each basin has one submerged turbine aerator to achieve complete mixing and oxygen transfer. Three rotary lobe positive displacement air blowers shown on Figure 4 are used to generate the supply of air to the submerged turbine aerator. The aeration-clarification configuration shown

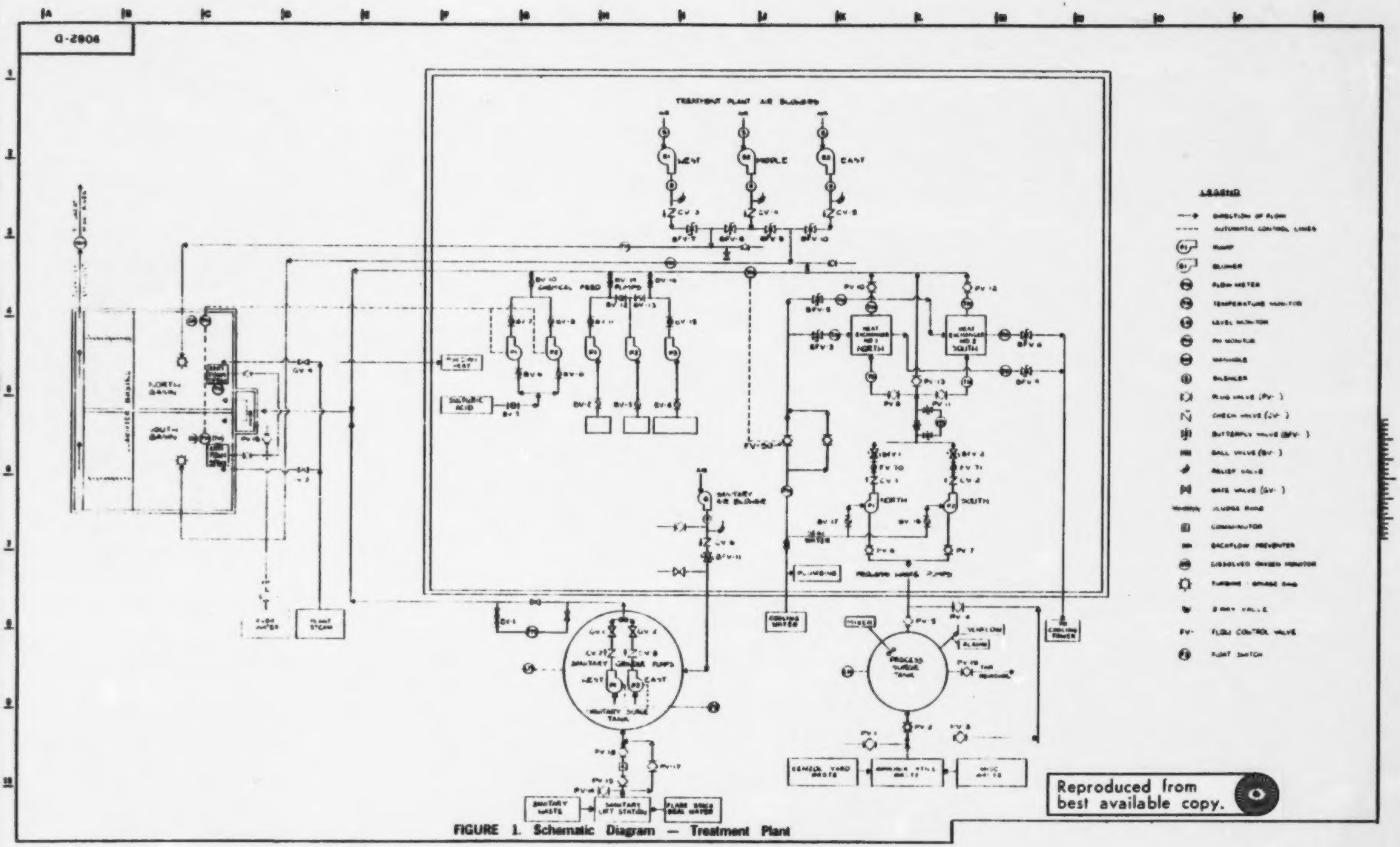

FIGURE 1. Schematic Diagram — Treatment Plant

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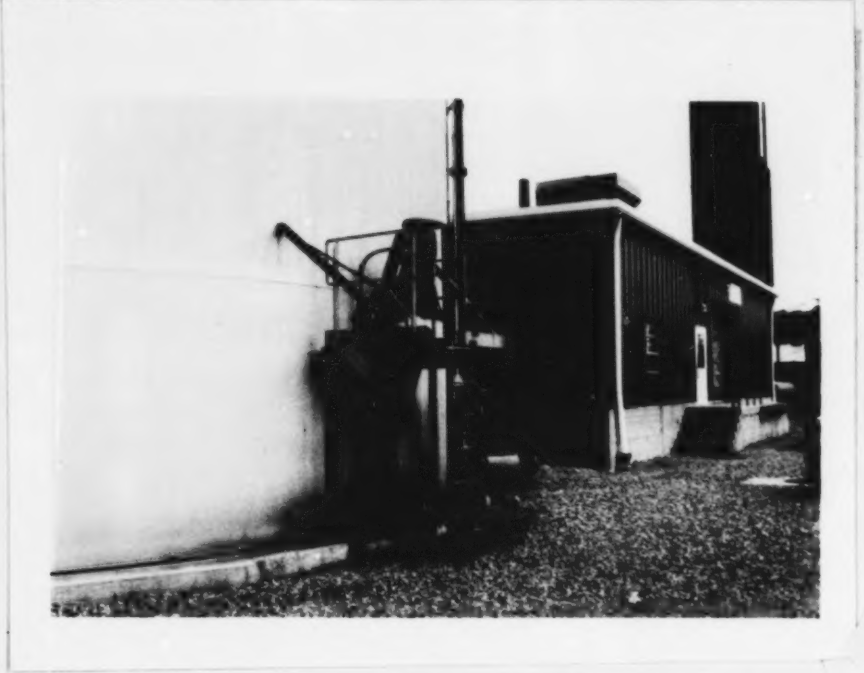

Figure 2. Process Surge Tank with Side Entering Mixer

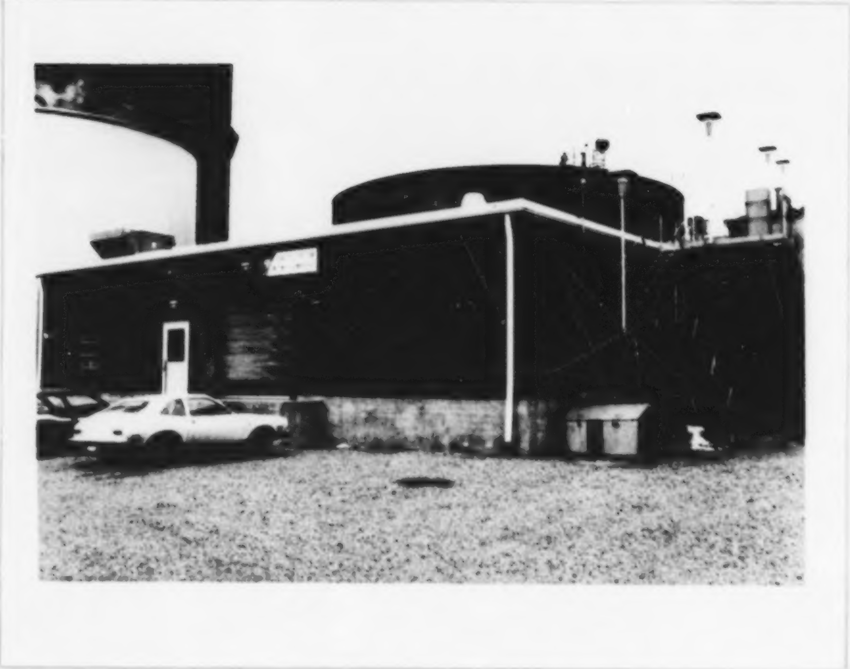

Figure 3. Control Building and Surge Tanks

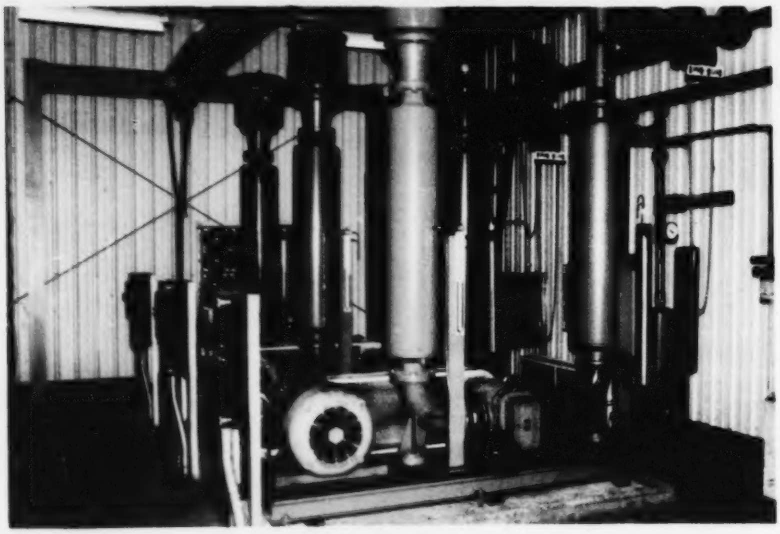

Figure 4. Positive Displacement Air Blowers

on Figure 5 allows the aerator to develop a horizontal velocity along the surface of the aeration basin. This, in turn, causes a downward flow of approximately 10 times the once-through flow in the "chimney" or the space provided between the aeration section and the clarification section. The majority of this flow passes back into the aeration basin, carrying with it the solids settled in the clarifier section. This action provides a theoretical recycle rate of 200%. The flow into the clarifier is equal to the incoming waste. This flow enters at the bottom along the length of the clarifier, passes vertically up through the basin, and is finally discharged from the system. A scraper mechanism is used to move the settled sludge down the sloped clarifier bottom to the chimney area where it is resuspended and carried back to the aeration basin.

The treatment plant graphic control panel (see Figure 7) enables the operator to monitor the physical operations of the plant including flows, temperatures, tank levels, etc., and to make minor corrections as required. The system continuously monitors the aeration dissolved oxygen, temperature and pH and automatically controls the latter two. Based on these controls and chemical analysis made in the treatment plant laboratory, adjustments are made to the system.

Shakedown and Start-Up

The checking and testing of the system conducted during February and early March of 1979 went smoothly. The only major problems encountered were a bad vibration in the south aerator mixer and an excessive pressure drop in the air supply system. The pressure drop problem was easily corrected by a modification to the sparge ring, but the vibration problem was not fully corrected until late August. Additional construction delays were encountered in the ammonia still area and the benzol yard area so that those areas were not fully operational until July and September, respectively.

On March 14, 1979, the north basins and process surge tank were filled with clean water. Waste ammonia liquor was then discharged to the surge tank which resulted in an extremely dilute solution of feed stock. Approximately 20 gpm of this dilute feed was pumped into the aeration basin which had been seeded with approximately 3000 gallons of activated sludge from Middletown, Ohio's, POTW. During the following days, additional truckloads of sludge were pumped into the system until the mixed liquor was at 1200 mg/l MLTSS.

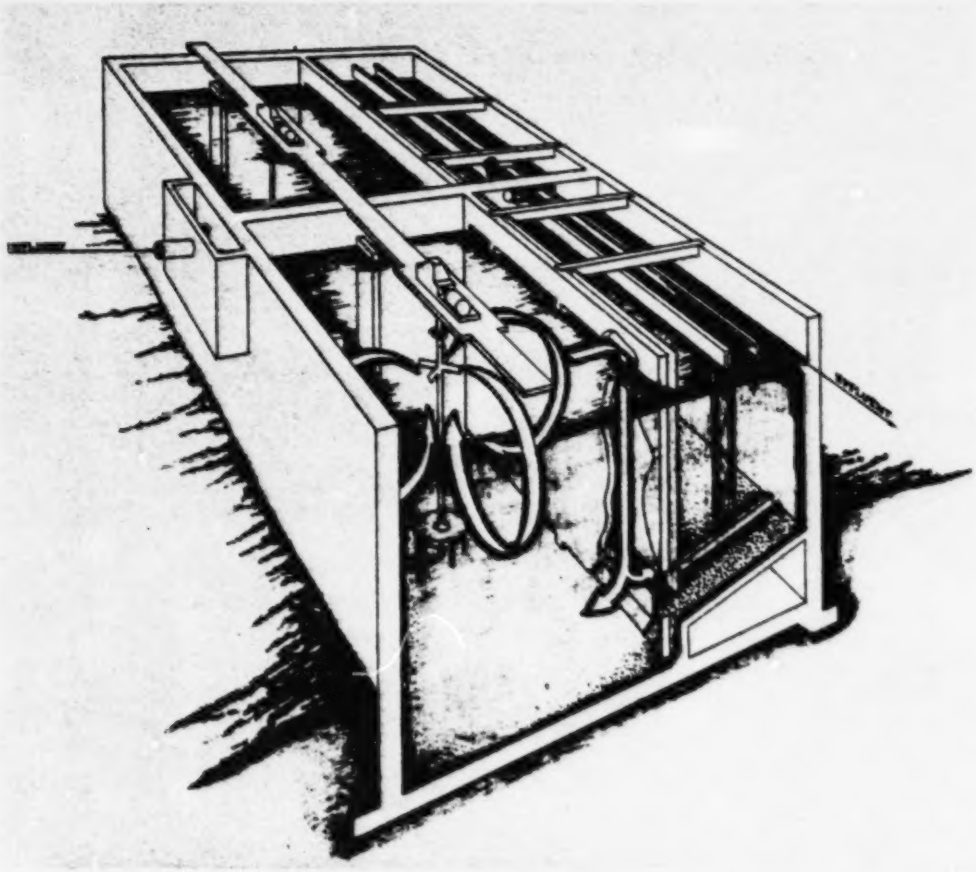

FIGURE 5. Schematic of Aeration / Clarification System

Figure 6. Waste Water Treatment Facility

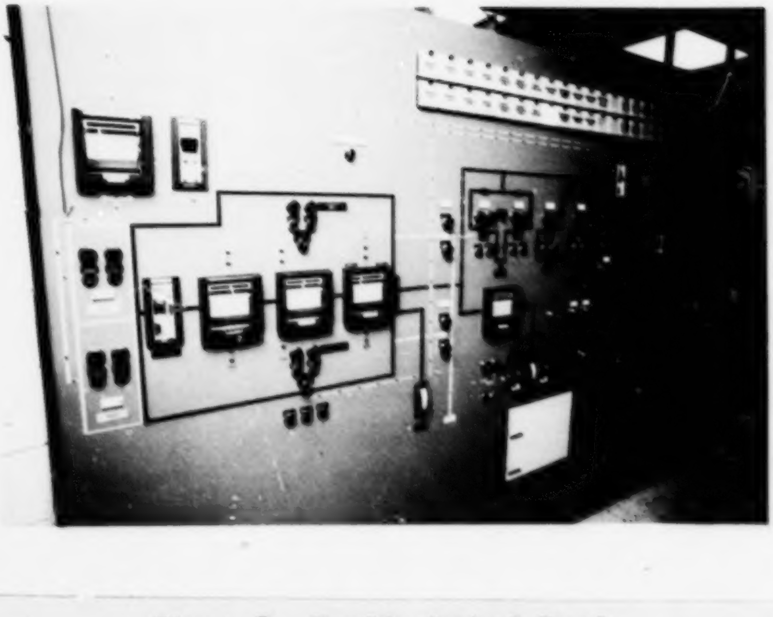

Figure 7. Graphic Control Panel

Because the Middletown POTW treats wastes from Armco's Middletown Coke Plant, the microorganisms were acclimated to coke plant waste. As shown on Figure 8, the total solids in the mixed liquor started to climb on day one and has continued to increase. At the end of thirty days, the mixed liquor had increased to 6000 mg/l and as shown on Figures 9 and 10, the total solids inventory has continued to climb while the volatiles have generally been above 70%. The dip in MLTSS concentration shown on Figure 10 is caused by the start-up of the second aeration basin after correction of the vibration problems and installation of a foam spray system. While operating with only one aeration basin, the system consistently removed phenol and thiocyanate with little or no removal of ammonia.

Discussion of Operating Data

Figure 11 shows the wastewater flows that have been treated in the first year of operation. The sharp increase in September is caused by the introduction of the benzol yard waste for the first time and the use of river water in a foam spray system. Because the system experienced severe foaming while operating on one basin, a river water spray header was installed around the basins to help knock down the foam. After the second aeration basin was started, and as the MLTSS continued to climb, the foam subsided allowing decreased use of river water during early 1980.

The system has functioned well in treating phenol even during upset or shock loading conditions. Figure 12 shows the phenol loadings that have been treated. The influent phenol monthly average has varied from a low of 80 kilograms per day (180#/day) to a high of 230 kg/day (500#/day) with no effect on the effluent quality. The highest monthly average discharge to date has been 30 grams per day (1 ounce per day).

Thiocyanate removal has not been as spectacular as is shown on Figure 13. Thiocyanate has proven to be the hardest parameter to remove and the most sensitive to varying operating conditions. For this reason, and the fact that the wet chemical test for thiocyanate is easy, it has been used to determine the relative health of the system. Figure 14 shows the daily influent and effluent concentrations during "upset" conditions. In May, phosphate concentrations in the system were inadvertently depleted. The phosphate levels were undetectable for more than a week before corrective measures were taken. Figure 14 shows the removal of thiocyanate was completely lost and recovered

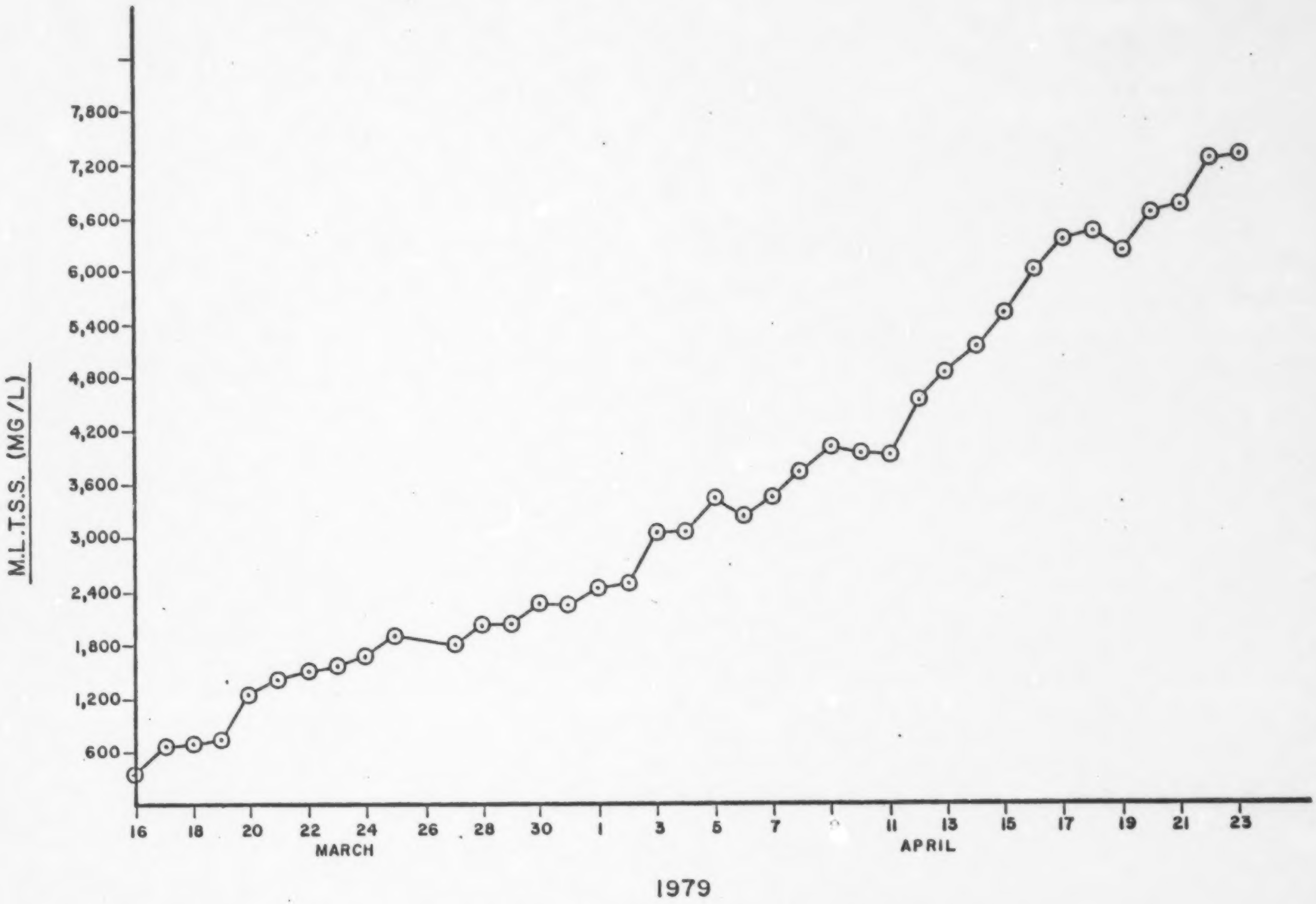

Figure. 8. Mixed Liquor Total Suspended Solids During Start-Up

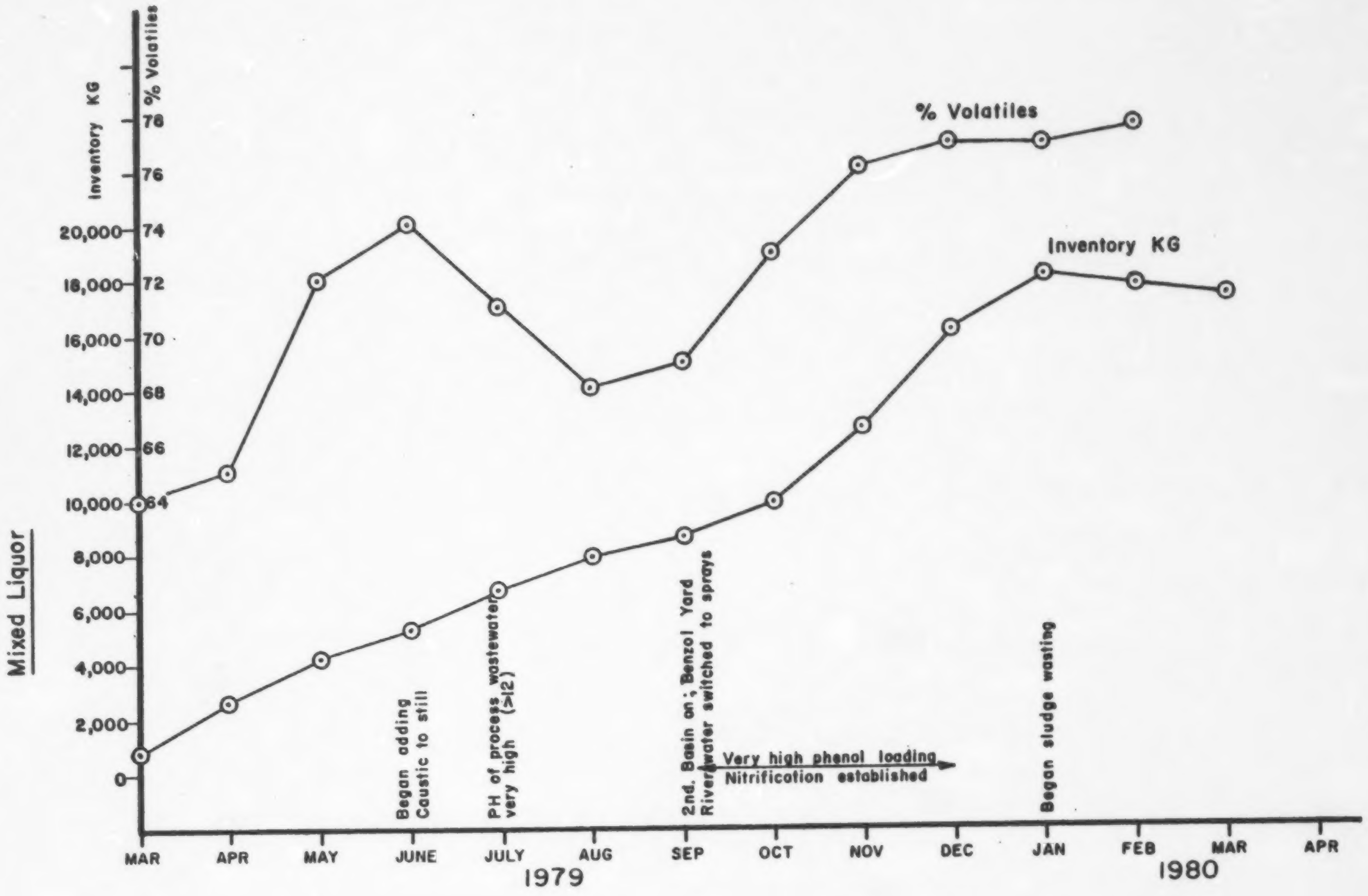

Figure 9. Mixed Liquor: Total BIO Mass Inventory & % Volatiles

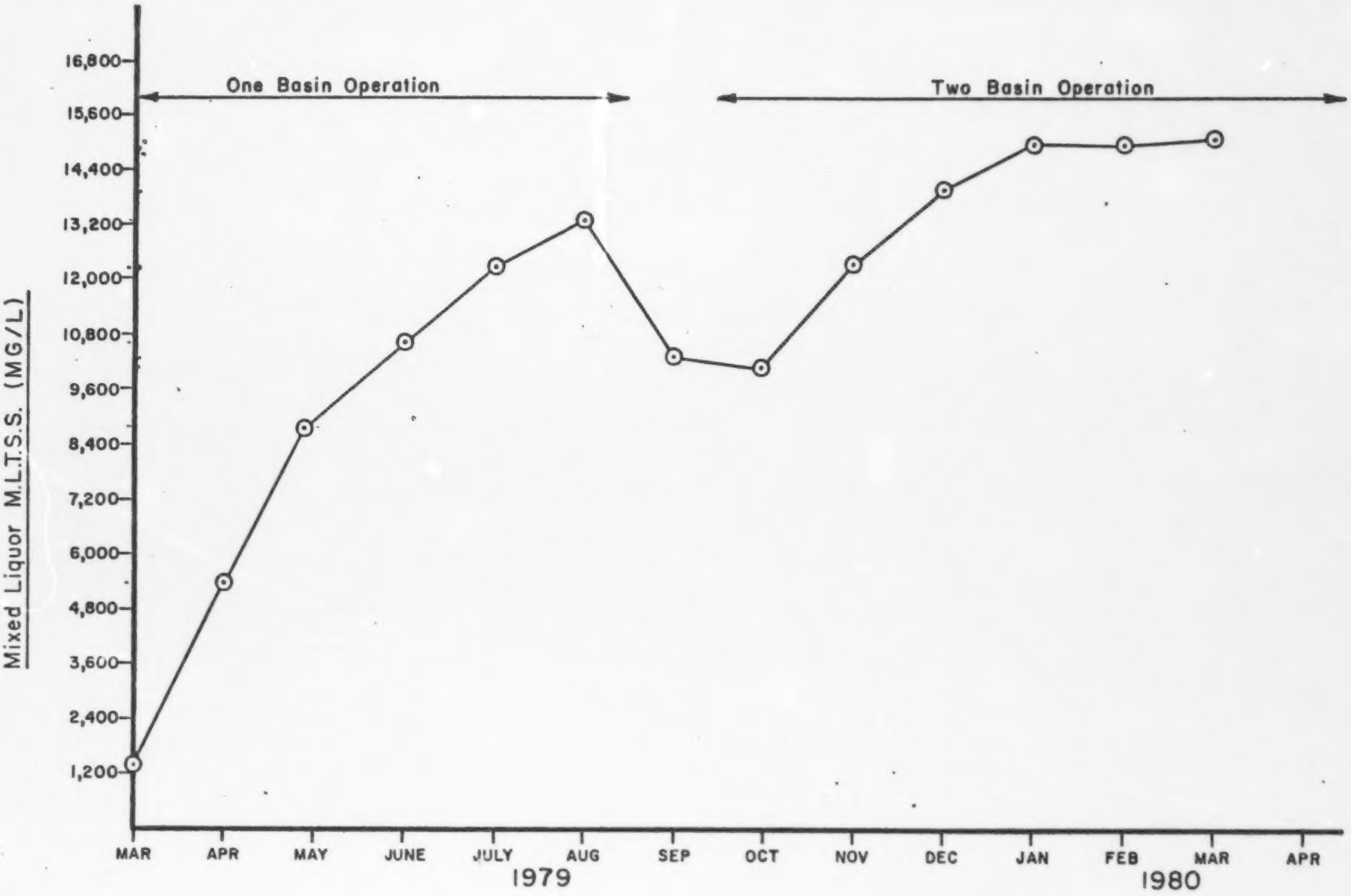

Figure 10. Mixed Liquor Daily Average Concentration M.L.T.S.S.

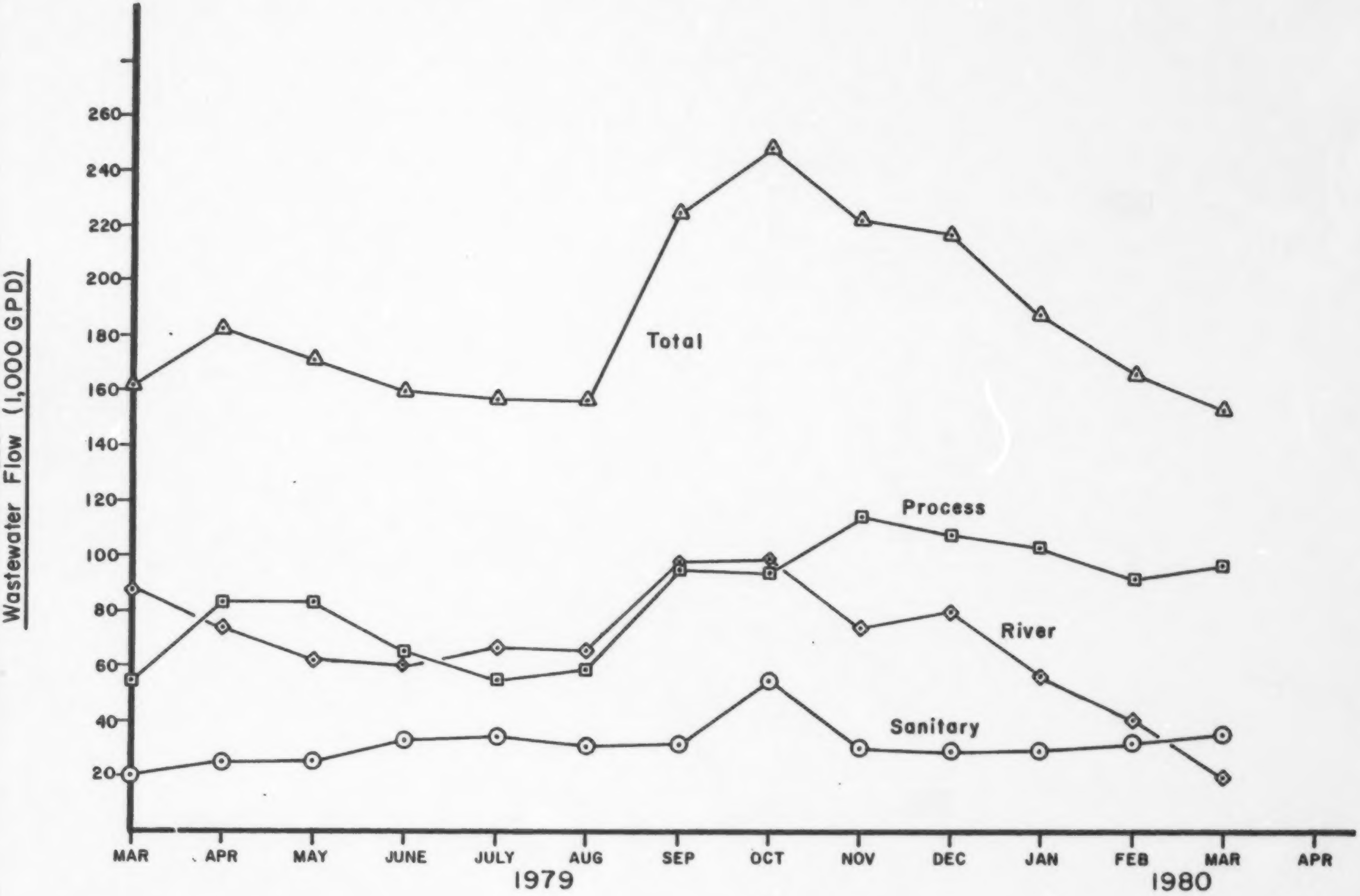

Figure II. Average Monthly Waste Water Flows

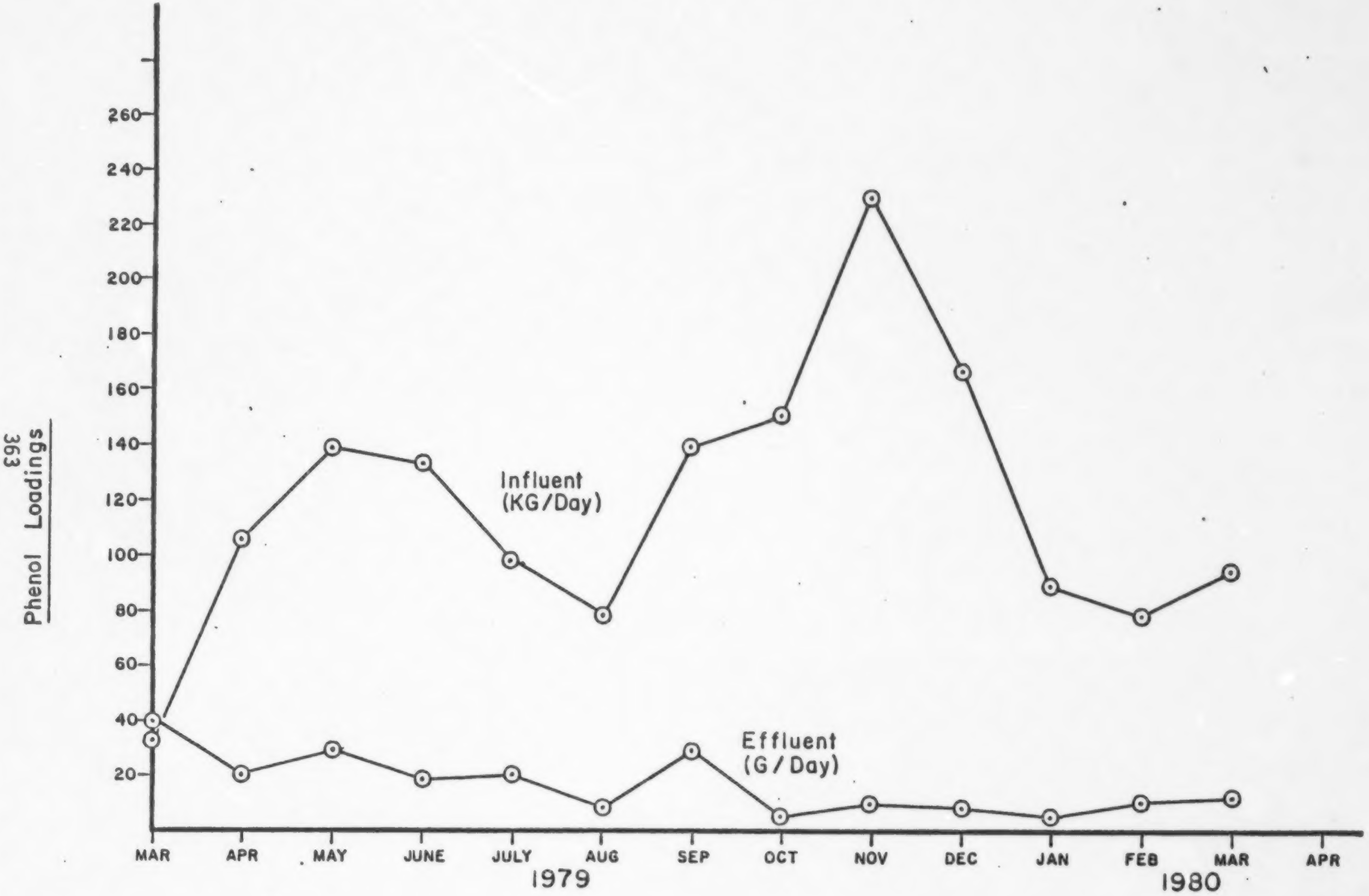

Figure 12. Phenols: Influent & Effluent Average Daily Loadings

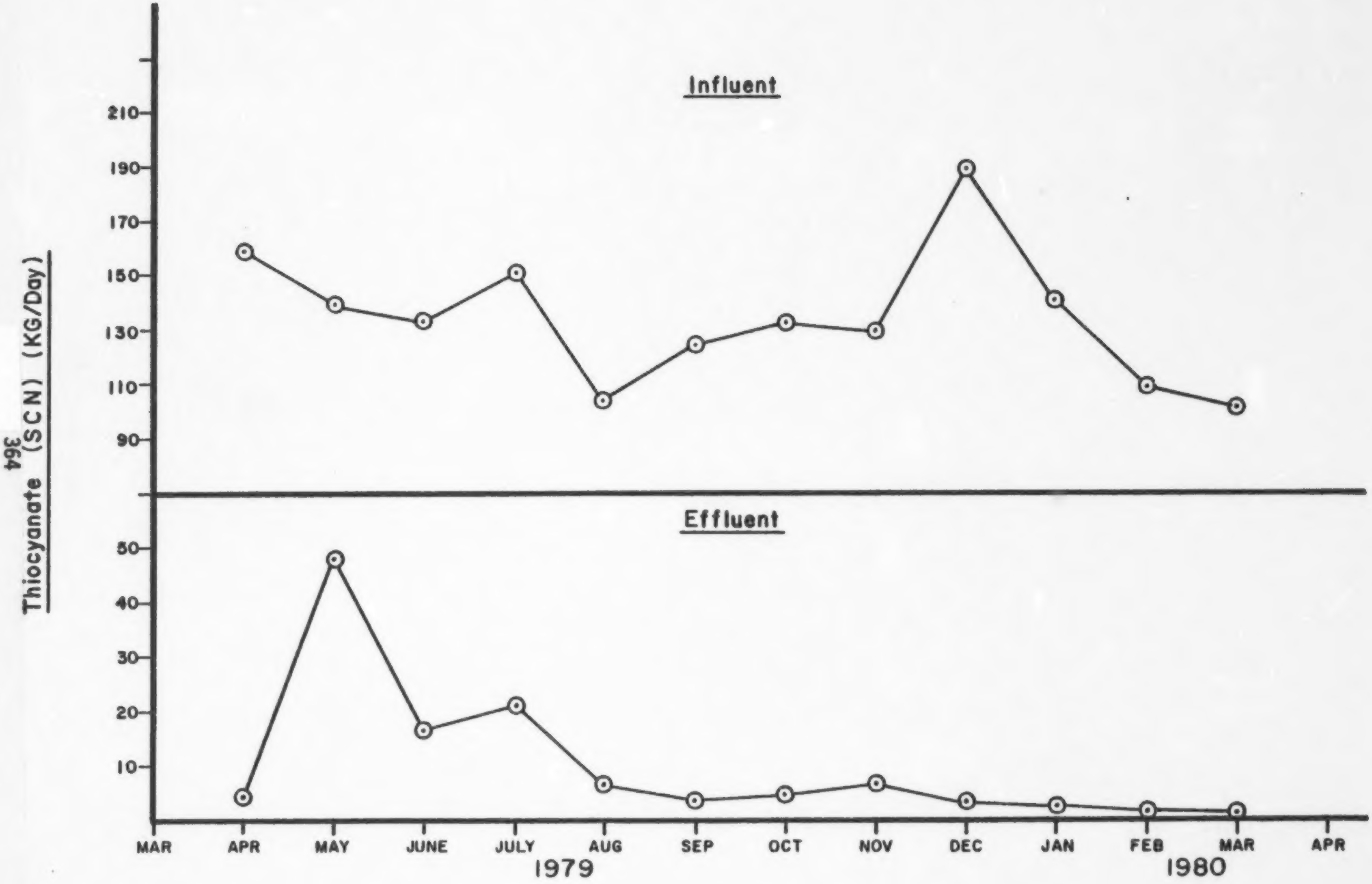

Figure 13. Thiocyanate (SCN)= Influent & Effluent Average Daily Loadings

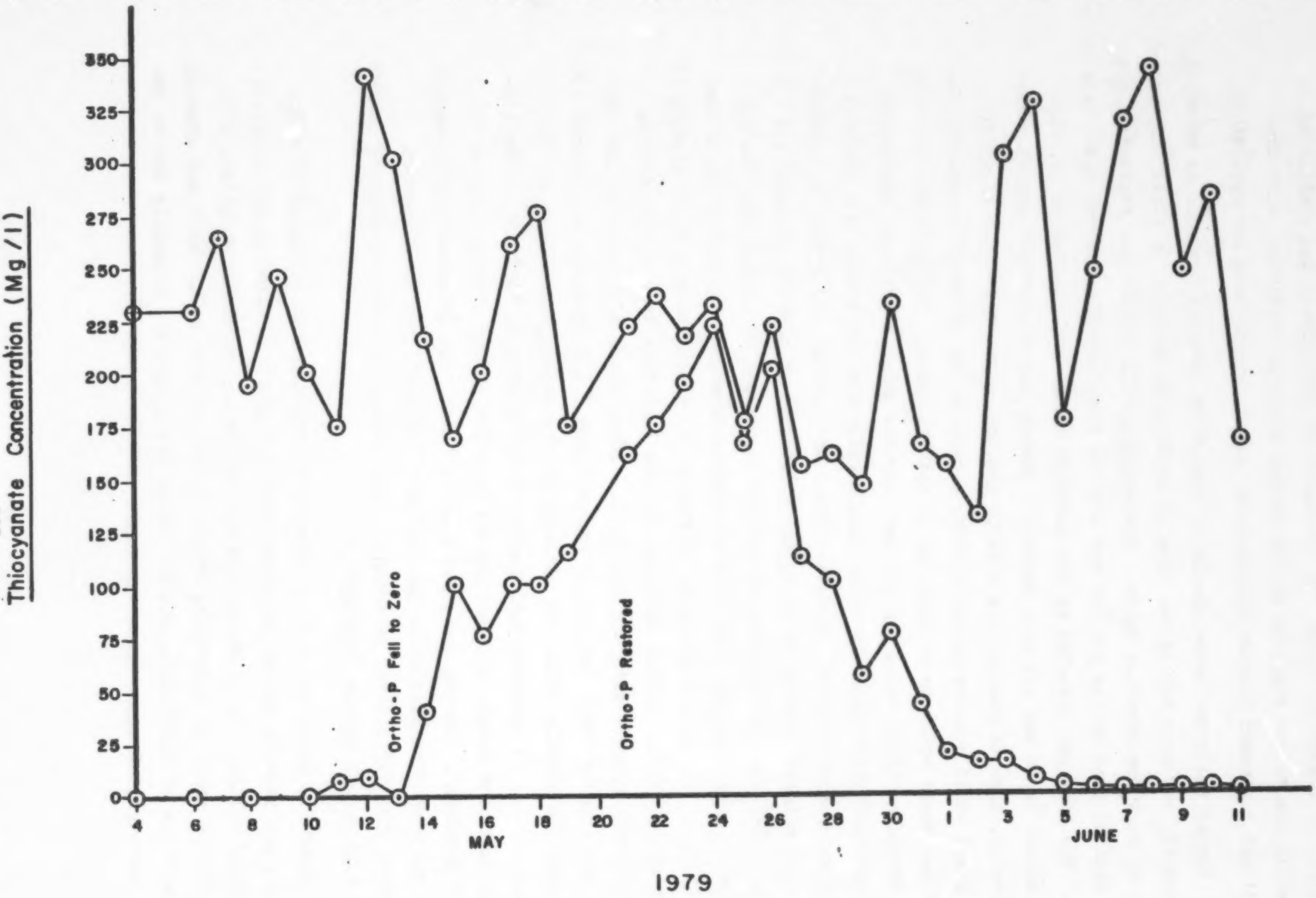

Figure 14. Upset Conditions Due To Lack Of Phosphorus Nutrient As Indicated By Thiocyanate

slowly. As Figure 13 shows, the treatment of thiocyanate has stabilized, possibly due to the start-up of the second basin in September, with the resultant increased biomass inventories, and no upsets have occurred since.

During the first seven months of operation, ammonia removal, as shown on Figure 15, was poor due to the lack of caustic in the ammonia still and operation of only one aeration basin. The ammonia still system was started before the caustic feed system and did not achieve fixed ammonia removal until late May. The bioplant operated on one aeration basin until September 15, when the second basin was put into service. During that four-month period, June-September, ammonia removal was erratic and the system difficult to operate. The plant would achieve nitrification, a drop in the pH would occur, and the next day there would be no evidence of nitrification. On September 15, 1979, the second aeration basin was put into service which stabilized the system. Soon nitrification began to occur consistently and the system has achieved excellent ammonia removal to date. Since mid-October the system has had an average influent loading of 85 kg/day (190#/day) of ammonia nitrogen and 130 kg/day (285#/day) of thiocyanate and has discharged an average for the six months of only 6 kg/day (13#/day) of ammonia-nitrogen. An indicator of the stability of the system is shown on Figure 16, which shows a shock loading in early March, 1980. Around February 29, the last free tray of the ammonia still became plugged with tar and pitch. After minor modifications and tuning, the standby still was put on stream March 5 and operated until March 18. Although the standby still did not exhibit the removal efficiency of the primary still, it operated well enough to bring ammonia loadings at the bioplant back into range, eliminating the need for backup storage lagoons or other treatment. During the first week of March, the treatment plant ammonia feed was more than tripled to 340 kg/day (750#/day), yet the biosystem achieved over 90% removal of ammonia. The highest quantity discharged during this time was 30 kg/day (66#/day).

Figure 17 shows the food-to-mass ratio expressed in kilograms of BOD_5, phenol, and ammonia fed to the plant over kilograms of mixed liquor volatile suspended solids. As is shown, the F:M ratios are currently very low, with BOD_5 in the range of 0.06 kg/kg MLVSS, phenol at 0.01 kg/kg MLVSS and ammonia in the range of 0.015 kg/kg MLVSS. These low ratios are primarily due to the high inventory of mixed liquor solids.

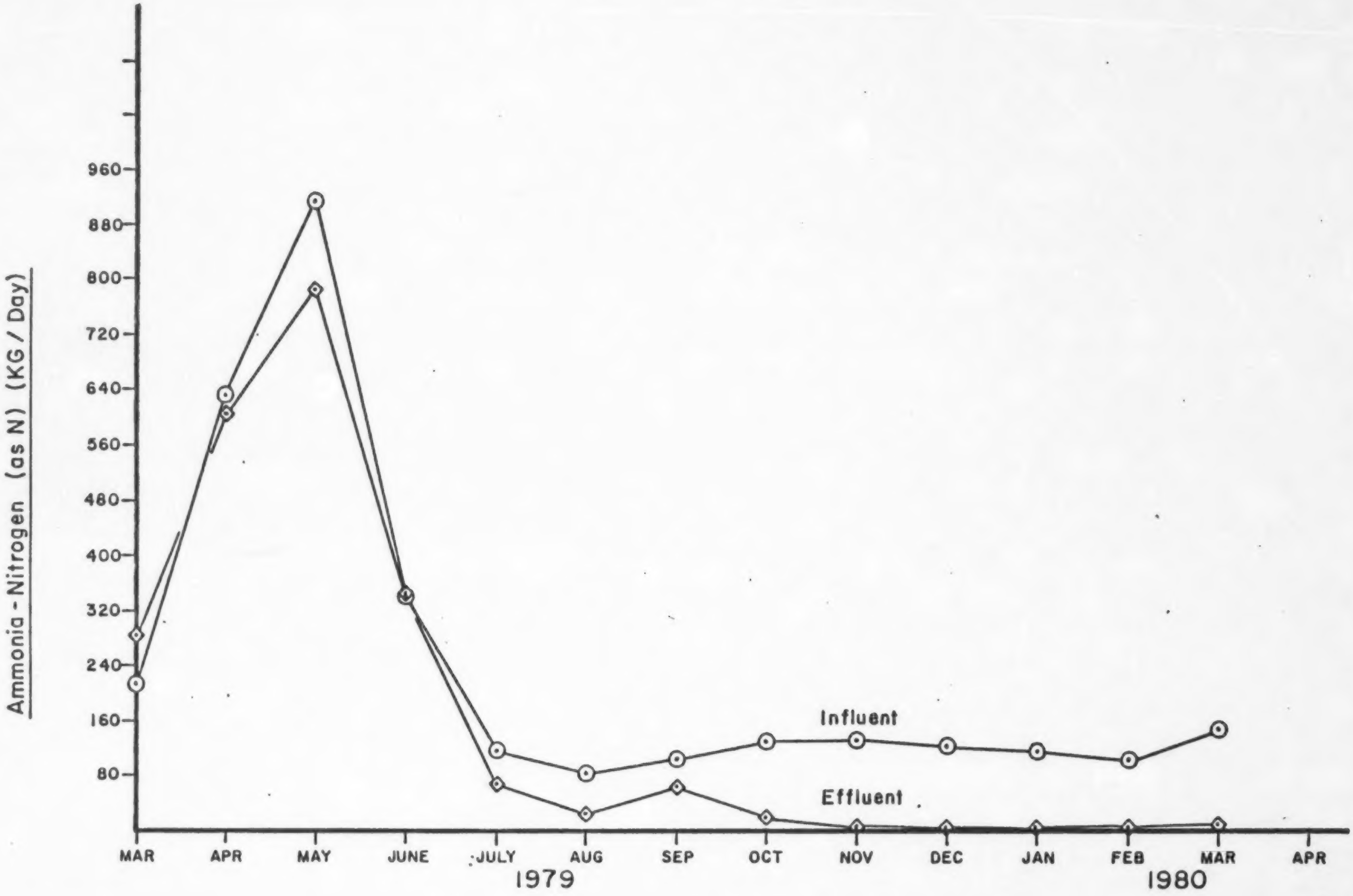

Figure 15. Ammonia Nitrogen = Influent and Effluent Total Daily Loadings

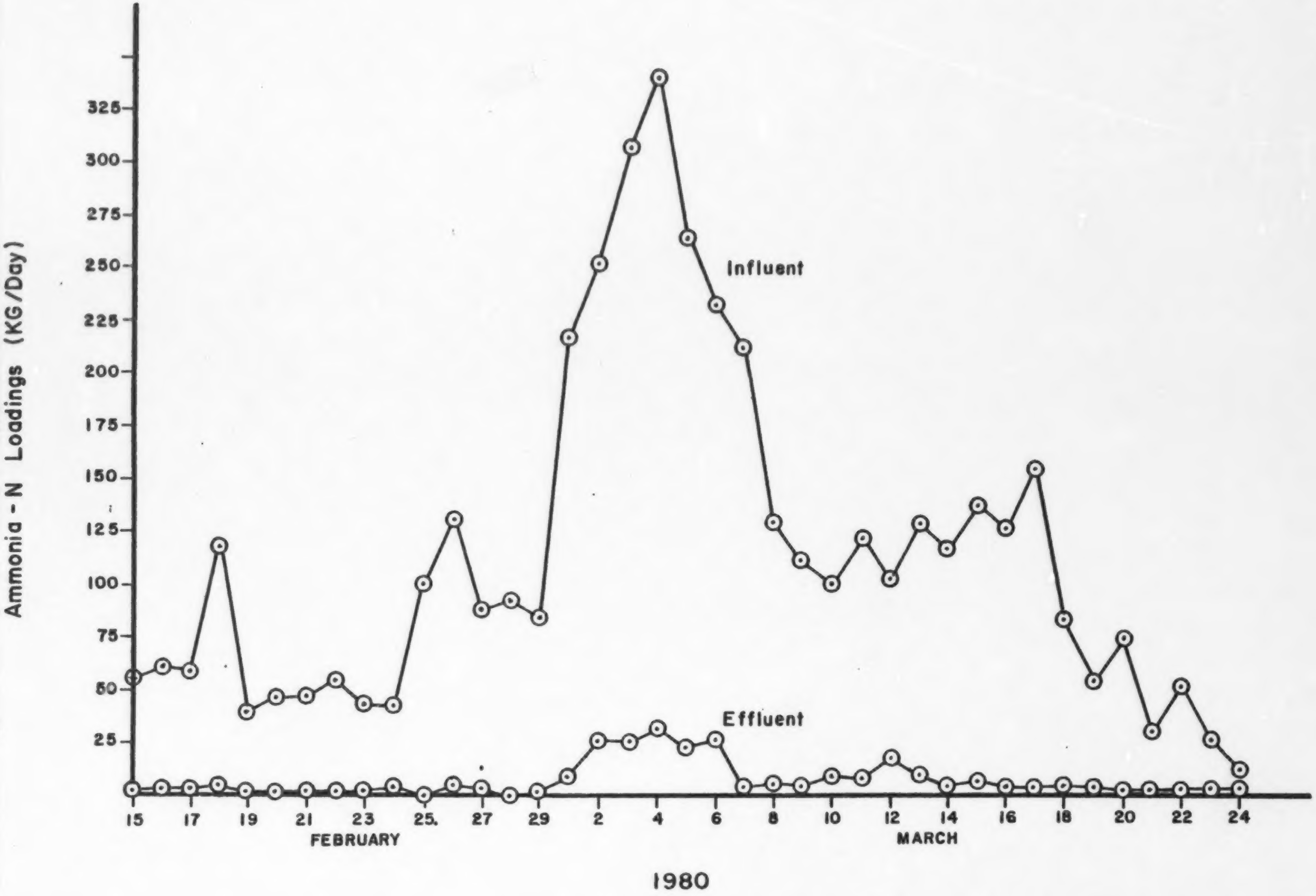

Figure 16. Ammonia Upset = Influent & Effluent Total Daily Loadings

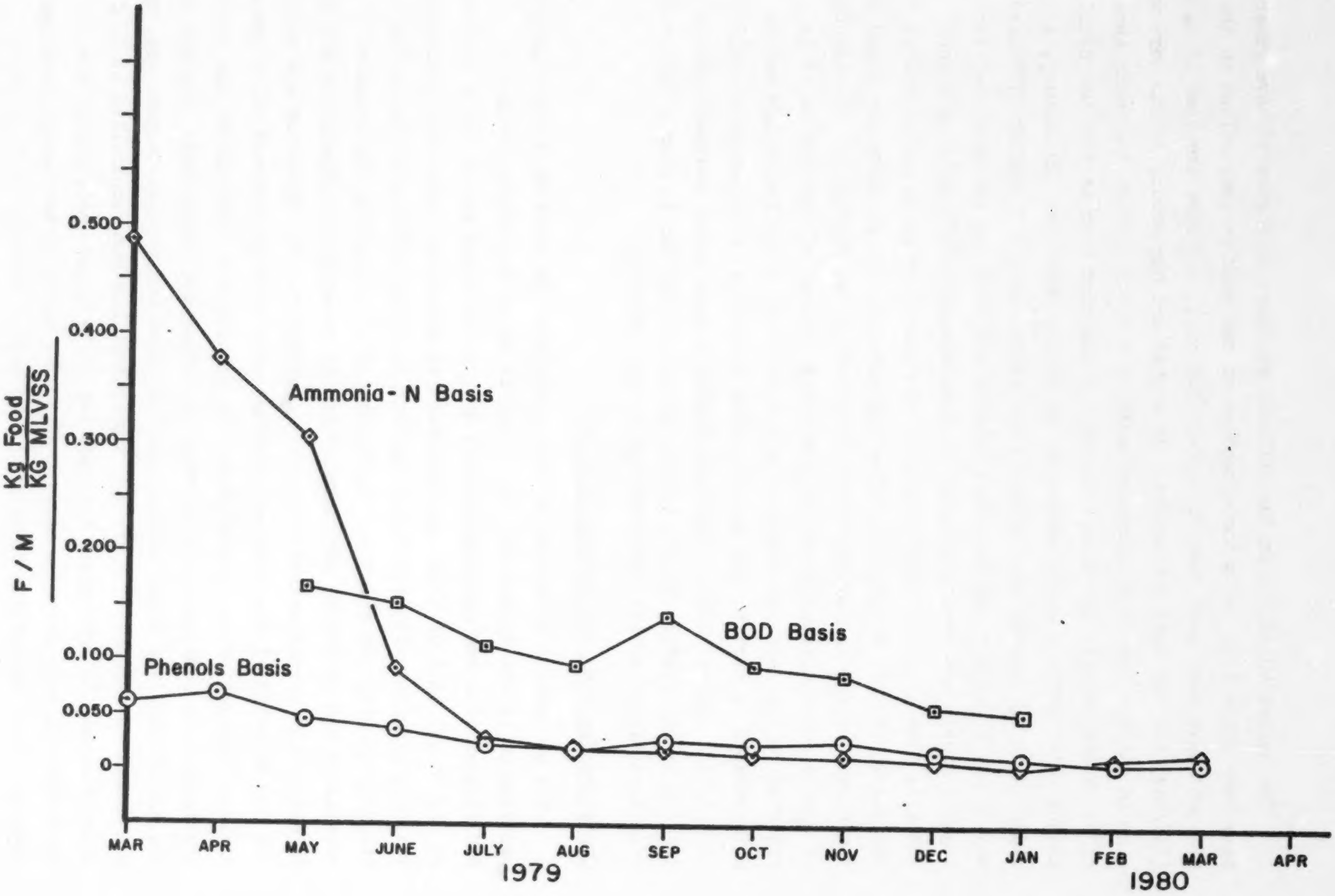

Figure 17. Food / Mass Ratios

The suspended solids in the effluent as shown on Figure 18 have generally been quite low. With the exception of one peak period, solids in the effluent have been less than 40 kg/day (90#/day), and have averaged 25 kg/day (55#/day) for the last six months. In August and September, solids were very high in the one operating aeration basin when flows through the basin were high. Subsequently, the sludge blanket in the clarifier section was nearly at the water surface and a carry-over of solids resulted. In January, a sludge wasting program was initiated and approximately 35 kg/day (77#/day) of solids are currently wasted. Mass balance calculations indicate that biological growth has been equivalent to approximately 0.25 kg/kg of phenol removal. The excellent performance in the clarifier is in part credited to the design of the integral clarification concept. No polymers are added and the flow receives no mechanical flocculation in the clarifier. The absence of sludge recirculation pumps has prevented breakup of the floc as it is returned to the aeration basin. The low effluent suspended solids may be attributable in part to the use of sodium hydroxide in the ammonia still rather than milk of lime. This contributes a much lower inorganic solids loading to the system, thus allowing the microorganisms to form a better floc with less "fine" solids carry-through to the effluent.

Operating Training and Responsibilities

The successful operation of this plant must be credited to outstanding performance by the operators. The plant is under the direct control of one day foreman with one operator present around the clock and an extra operator on day turns. All of these men underwent an extensive three-week classroom training program, with additional on-hand training before and during the start-up stages. In addition, the operators are obtaining the required experience and reviewing additional training material in preparation for obtaining State certification as licensed operators. The operators are conducting the majority of the chemical analyses with only cyanide and oil & grease analyses contracted to outside labs. By manning the plant around the clock, the various operations can be closely monitored and controlled. Figures 19, 20, and 21 show the close control that has been achieved on temperature, pH, and dissolved oxygen. The average temperature has been controlled at 25°C plus or minus 1°C throughout the last year. By close observation, the operators can make corrections in the cooling water system before troubles develop. Even though the pH on Figure 20 varies from 6.6 to 8.3, the

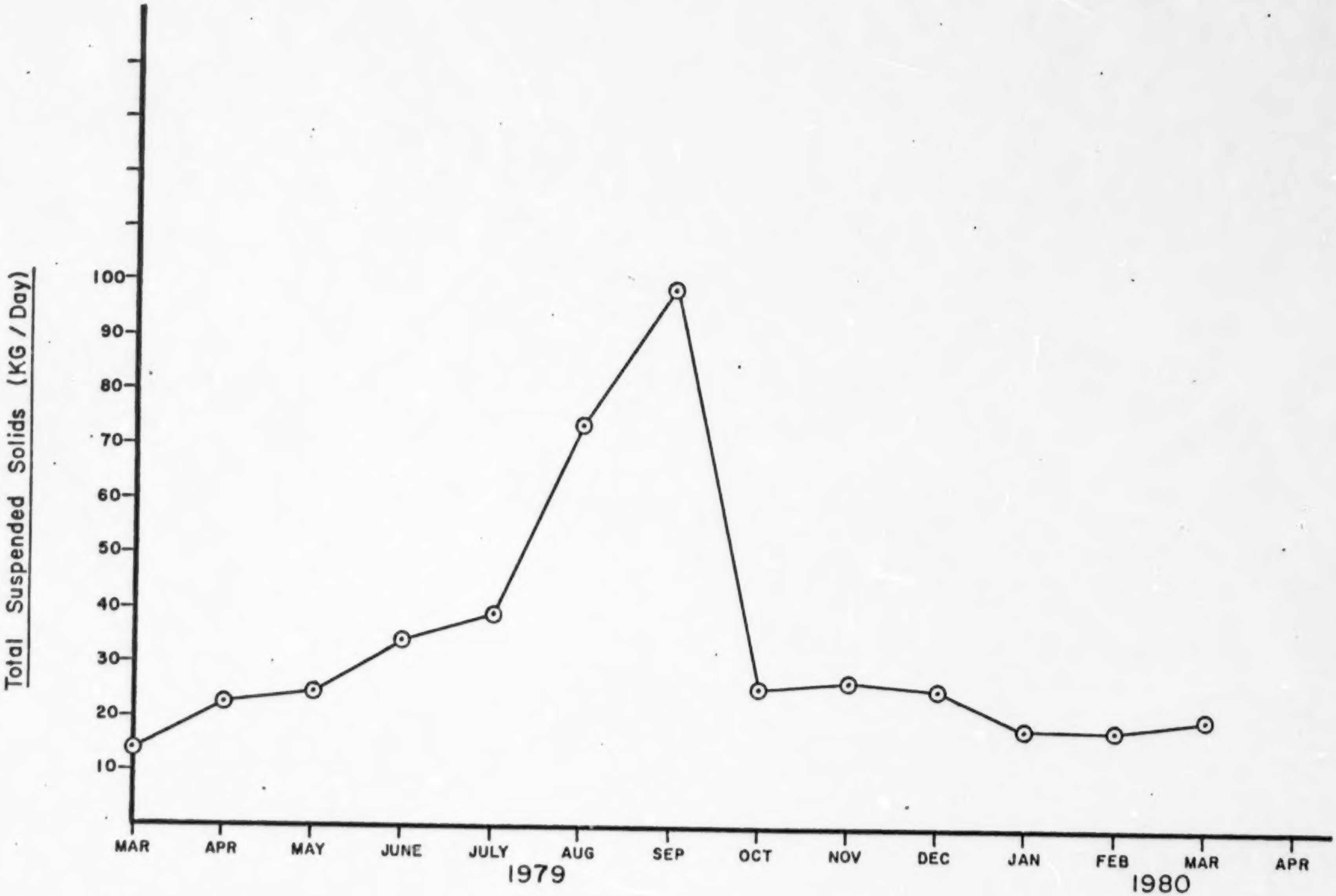

Figure 18. Effluent Total Suspended Solids Average Daily Discharge

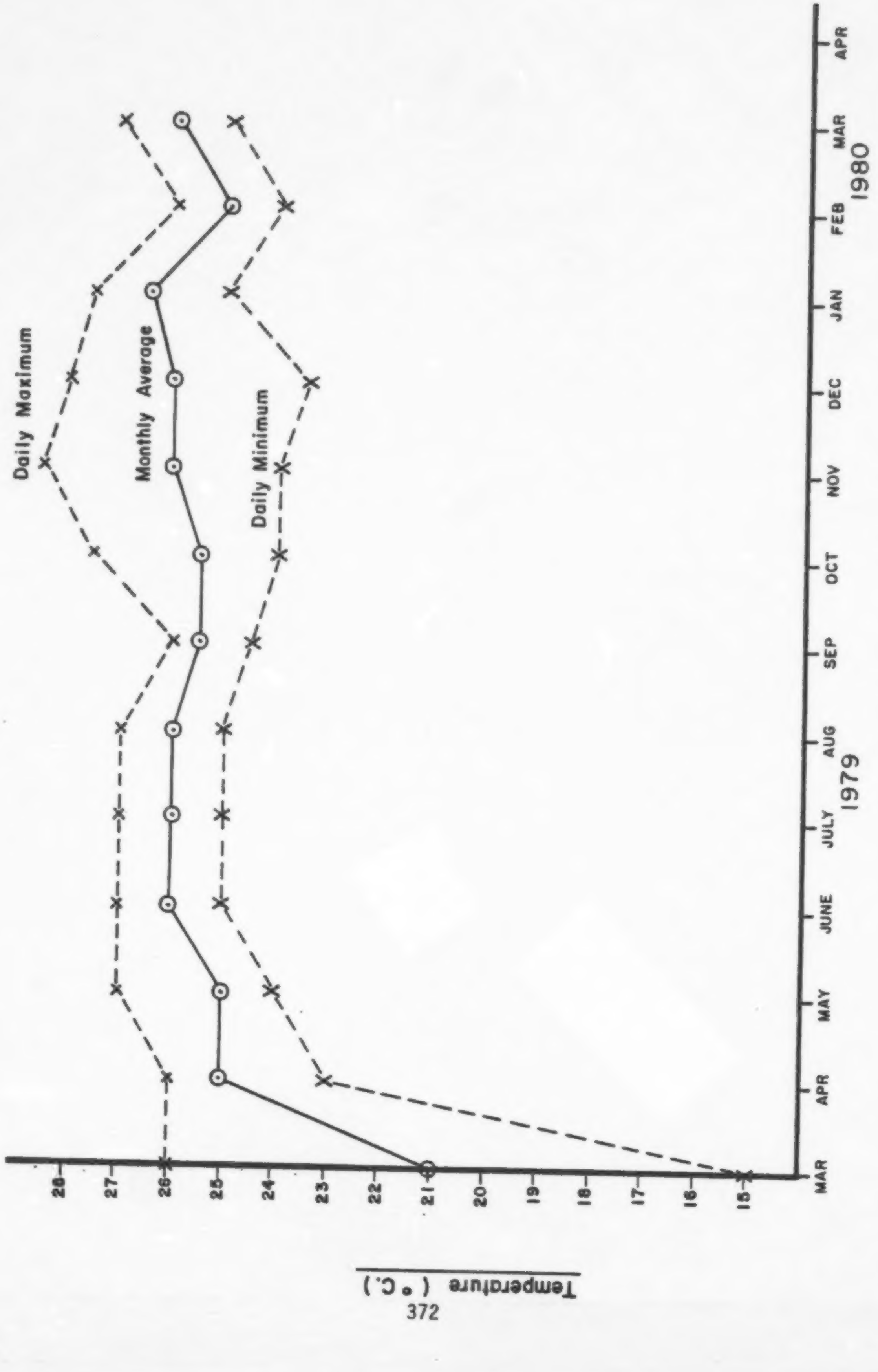

Figure 19. Aeration Basin Temperature

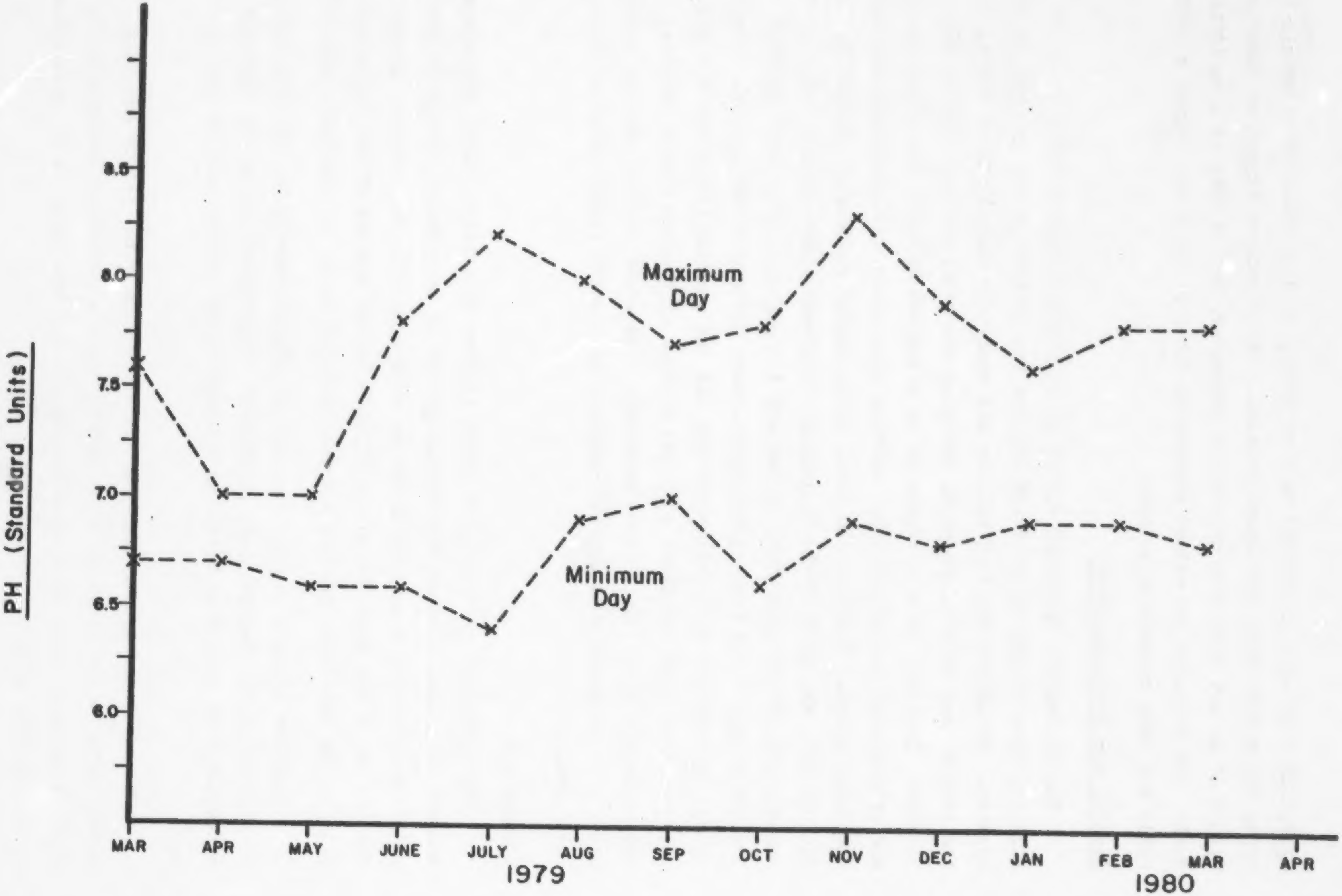

Figure 20. Aeration Basin Maximum & Minimum PH Data

operators were able to correct this by adding acid or alkaline materials to bring the system back into specification. The dissolved oxygen as shown on Figure 21 is not usually a controlled parameter, but is used as a monitoring tool. The operator can detect changes in the D.O. which may signal a pending upset and take corrective action.

Capital and Operating Cost

The biological treatment system as originally constructed cost $2.15 million, with an additional $1.35 million for collection and ammonia still systems. An additional $1.5 million was spent for miscellaneous sumps, cooling towers, and related projects, bringing the total project cost to $5.0 million. Included in this figure is an estimated $800,000 for modifications and relocations to retrofit the existing coke plant to accommodate the new treatment plant. Based on the total contaminated wastewater design flow of 140,000 GPD, the cost of the biological treatment plant was $15/gallon. The ammonia stills and collection system add $10/gallon, for a total capital cost for the bioplant and associated pretreatment systems of $25/gallon. Direct operating cost for the treatment plant and the ammonia stills for the period July-December 1979 was about $18/1000 gallons of process liquor treated, or approximately $1.30/ton of coke produced. The added cost of capital recovery makes the treatment cost $30/1000 gallons of process liquor or $2.20/ton of coke produced.

Conclusions

The treatment of coke plant waste liquors to achieve phenol and ammonia removal in a single stage reactor has proven to be a viable treatment method, although expensive when used in series with a caustic soda ammonia still. Control of pH has been the most difficult factor because of the formation of acid in the treatment process and the destruction of the available alkalinity.

Negative effects on nitrification or phenol removal by the introduction of emulsified oil has not been a problem. Emulsified oil in the effluent is averaging less than 5 mg/l with an average inlet loading rate of over 40 mg/l.

Operating the system with the extremely high mixed liquor and long sludge ages in the aeration basin has not been a problem. During periods of high flow, some carry-over of solids is evident but there is no indication of a problem during normal operations.

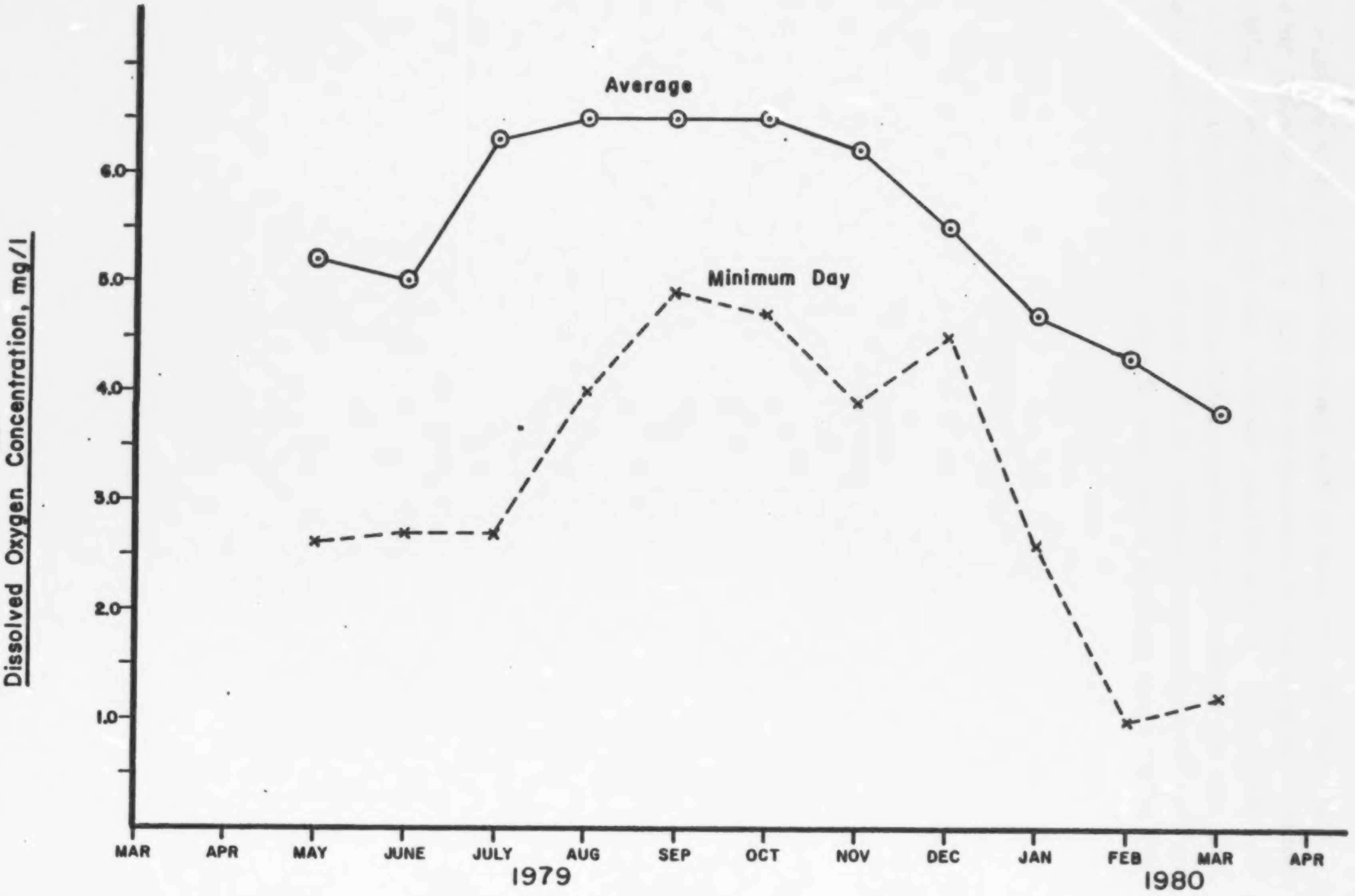

Figure 21. Aeration Basin Dissolved Oxygen Data

Although the operations of this plant have been extremely smooth, a degree of caution must be exercised if this data is to be considered for other treatment plants. At this writing, the plant has operated thirteen months with only six months of satisfactory nitrification. Nitrification has only occurred during the winter months. It is essential for complete demonstration of the plant to obtain a full year of operating data.

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TREATMENT OF COKE PLANT WASTEWATER USING PHYSICAL-CHEMICAL AND BIOLOGICAL TECHNIQUES

By

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ABSTRACT: Pilot studies were performed concurrently at two coke plants to investigate the effectiveness of physical-chemical and biological treatment in meeting steel industry BAT guidelines for the by-product cokemaking subcategory.

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TREATMENT OF COKE PLANT WASTEWATER USING PHYSICAL-CHEMICAL AND BIOLOGICAL TECHNIQUES

INTRODUCTION

The primary purpose of this project was to investigate the technical and economical feasibility of treating by-product cokemaking wastewater to Best Available Technology (BAT) levels using physical-chemical and biological methods. The wastewaters generated from the by-product recovery process include excess ammonia liquor, benzol plant wastes and other miscellaneous discharges associated with the production of coke. Pollutants contained in these wastewaters typically include suspended solids, ammonia, phenolic compounds, cyanide, sulfide, thiocyanates, oil and greases as well as many toxic pollutants. Two plants were studied; the physical-chemical test work was performed at Shenango, Inc., Pittsburgh, Pa.; the biological study was conducted at the Wheeling-Pittsburgh Steel Corp., Follansbee, W.V.. The plants investigated had operating treatment systems for upgrading the raw wastewater to a Best Practical Control Technology (BPT) Currently Available level.

The investigations were conducted using the U.S. Environmental Protection Agency's (EPA's) mobile physical-chemical and biological treatment systems. These pilot plants are housed in three semi-trailer vans as shown in Figures 1-3.

EXPERIMENTAL RESULTS (PHYSICAL-CHEMICAL RESEARCH SITE)

General

The physical-chemical investigation on Shenango's by-product cokemaking wastewater was conducted between November 14, 1979 and January 17, 1980. During the study, coke production averaged 1,673 metric tons (1,519 tons) per day, while the average wastewater flow was 1,025 m^3/day (0.271 mgd). The corresponding water application rate (liters of water/metric tons of coke produced) during the study was 743 liters/kkg (178 gal./ton). Based on BAT limits, the allowable pollutant concentrations in the effluent would be:

Parameter	BAT Limit
pH	6.0-9.0
Ammonia, mg/l	13.4
Cyanide-T, mg/l	0.33
Oil and Grease, mg/l	13.4
Phenol, mg/l	0.27
Sulfide, mg/l	0.4
Suspended Solids, mg/l	27
Thiocyanate, mg/l	200

EPA TRAILERS

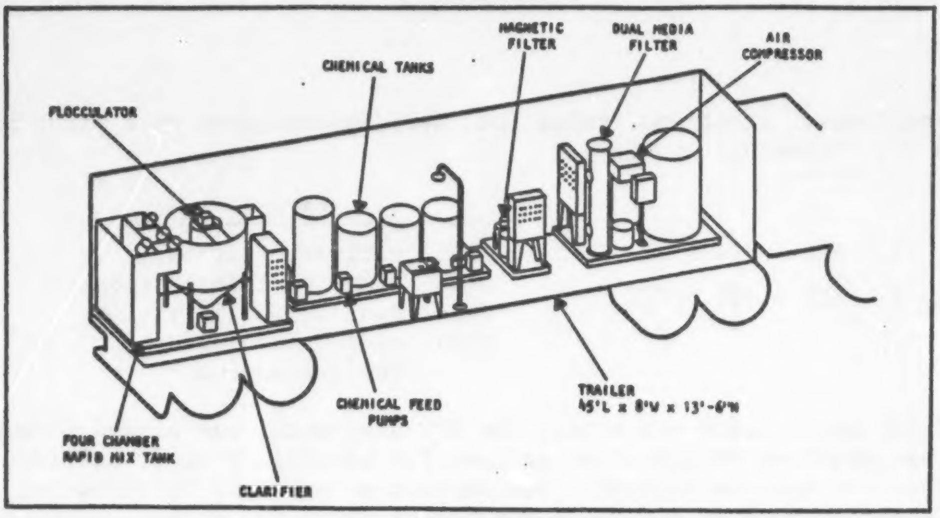

Figure 1.

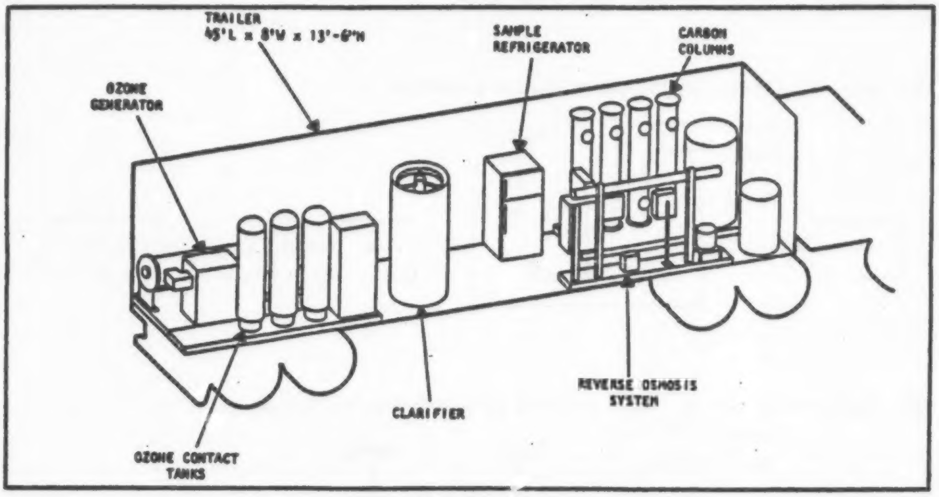

Figure 2.

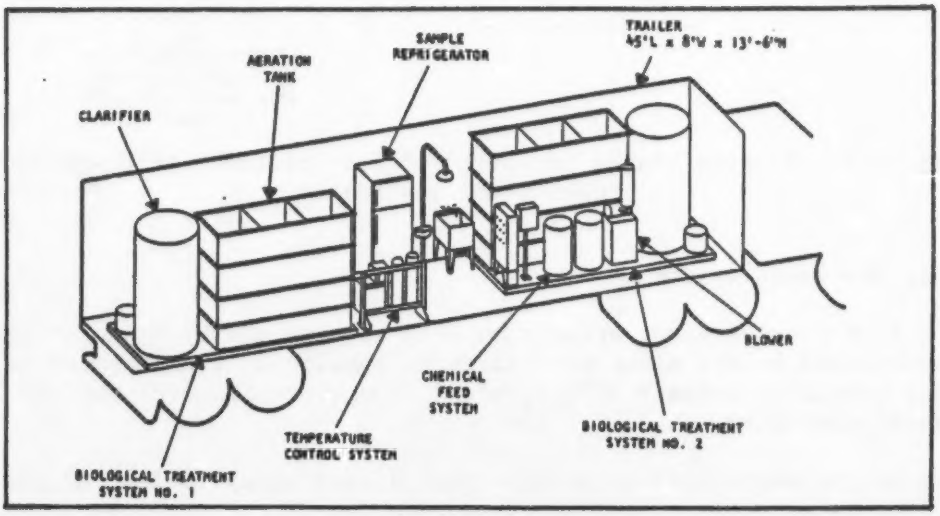
SAMPLE REFRIGERATOR
TRAILER 45'L x 8'W x 13'-6"H
AERATION TANK
CLARIFIER
BLOWER
CHEMICAL FEED SYSTEM
BIOLOGICAL TREATMENT SYSTEM NO. 2
TEMPERATURE CONTROL SYSTEM
BIOLOGICAL TREATMENT SYSTEM NO. 1

Figure 3.

The advanced waste treatment trains that were investigated on a pilot scale included the following:

1. ACL + FIL + AC
2. ACL + SBD + FIL

KEY

AC: activated carbon
ACL: alkaline chlorination
FIL: dual media filtration
SBD: sodium bisulfite dechlorination

In the first pilot treatment train, the BPT wastewater was passed through a two stage alkaline chlorination process for cyanide, phenol, sulfide, thiocyanate and ammonia removal. The wastewater was then filtered for suspended solids removal and dechlorinated on activated carbon. The second treatment train again consisted of alkaline chlorination which was followed by sodium bisulfite dechlorination and dual media filtration. The treatment train arrangements are shown in Figure 4.

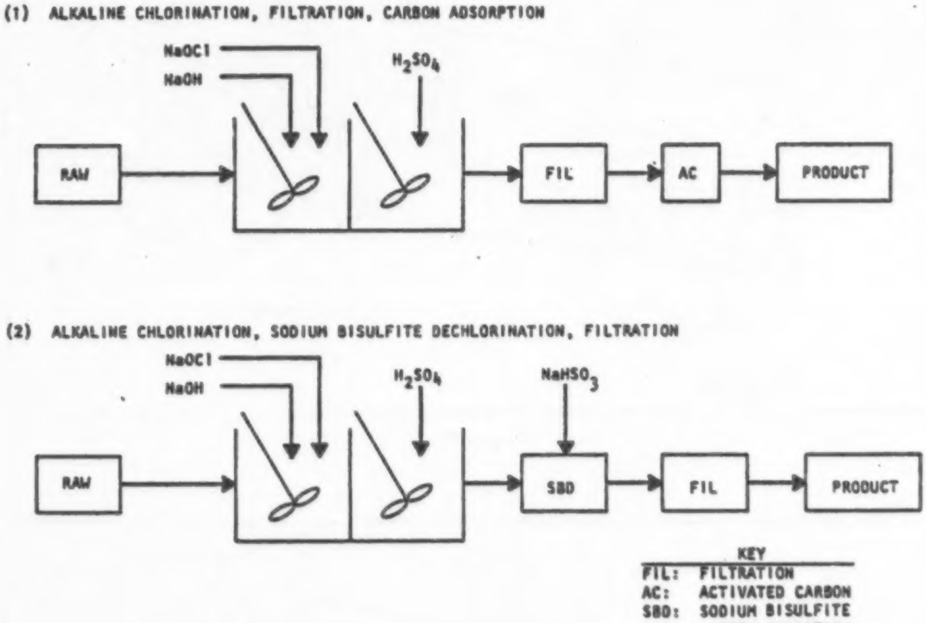
(1) ALKALINE CHLORINATION, FILTRATION, CARBON ADSORPTION
NaOCl
NaOH
H_2SO_4
RAW
FIL
AC
PRODUCT
(2) ALKALINE CHLORINATION, SODIUM BISULFITE DECHLORINATION, FILTRATION
NaOCl
NaOH
H_2SO_4
$NaHSO_3$
RAW
SBD
FIL
PRODUCT
KEY
FIL: FILTRATION
AC: ACTIVATED CARBON
SBD: SODIUM BISULFITE DECHLORINATION

Figure 4. Process trains investigated for treatment of by-product coke plant wastewater.

Wastewater Treatment System

There are four process water streams associated with the by-product cokemaking operations at the plant investigated; namely (1) final cooler wastewater; (2) phenolate wastes; (3) light oil separator effluent; and (4) hot oil decanter underflow.

The final cooler wastewater originates from direct spray cooling of the coke oven gas and represents about 31 percent of the total plant flow. The phenolate waste stream (excess flushing liquor) is passed through a free ammonia still, dephenolizer and a fixed ammonia still prior to mixing with other plant wastes. This stream comprises 47 percent of the combined coke plant flow. The hot oil decanter discharge (~19% of plant flow) passes through a dissolved-air flotation unit, containing 4.6 m^2(50 ft^2) of surface area. The underflow is then blended with other plant effluents. The fourth major process stream, the light oil separator effluent, accounts for approximately three percent of the coke plant effluent flow. The discharges from these four principal coke plant wastewater sources are combined and blended in a 643 m^3 (170,000 gal.) equalization tank equipped with mechanical mixers. The equalized effluent, representing a BPT wastewater, is then fed to a full-scale advanced waste treatment system. Feedwater to the mobile system was taken out of the equalization basin during the entire study.

Characteristics of the wastewater obtained from the equalization basin during the study are shown in Table 1.

TABLE 1. COMPARISON OF BPT EFFLUENT LIMITATION GUIDELINES TO ACTUAL PLANT VALUES OBSERVED DURING THE STUDY PERIOD

Parameter	BPT[1] Limit	Analytical Value From the Research Site Average	 Range
Cyanide T, mg/l	29	85.2	4.7-267.5
Phenol, mg/l	2	142	68-850
Ammonia, mg/l	123	506	101-2,150
Oil and Grease, mg/l	15	54	3-147
Suspended Solids, mg/l	49	103	26-361
pH	6.0-9.0	-	3.8-10.8

[1] Dev. Doc., By-Product Cokemaking - EPA 440/1-79/024a, Oct. 1979

As shown in the table, concentrations of pilot system feedwater were well above the BPT limits during the study.

Alkaline Chlorination Results

During the study, 40 alkaline chlorination test runs were performed. The pilot test procedure consisted of passing the coke plant wastewater through a series of completely mixed reaction tanks under alkaline and neutral pH conditions in the presence of an oxidizing agent (sodium hypochlorite). In the first reaction tank, sodium hydroxide and sodium hypochlorite were added to the wastewater to oxidize the cyanide present to cyanate. In the second chamber, the wastewater was neutralized in the presence of excess chlorine to oxidize ammonia. The treated wastewater was then filtered and dechlorinated using either activated carbon or sodium metabisulfite. As a byproduct of treatment, other parameters exerting a chlorine demand (sulfide, phenol, thiocyanate, etc.) were also oxidized.

The alkaline chlorination system was run continuously over the test period to provide 24 hour composite samples for both conventional and toxic analysis. Feed ammonia concentration ranged from 100 mg/l to a high of almost 2,200 mg/l during the study. However, effluent ammonia was typically less than 10 mg/l as shown in Figure 5. A summary of selected alkaline chlorination test results is shown in Table 2. Figure 6 indicates that effluent ammonia was reduced significantly as the oxidation-reduction potential (ORP) setting was increased. Operating in the 800-950 mv range provided sufficient treatment while maintaining the lowest possible chlorine residual. The data presented in Table 2 indicate that alkaline chlorination was effective in reducing pollutant concentrations to below BAT levels with the exception of total cyanide. Obviously, the presence of complexing agents in the coke plant effluent prevented complete oxidation of the cyanide by chlorine.

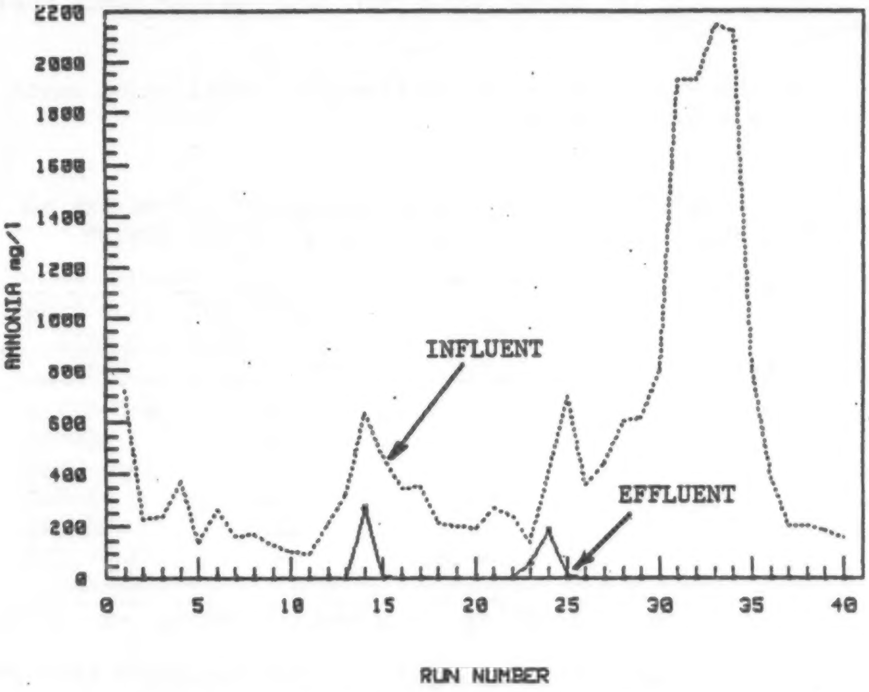

Figure 5. Alkaline chlorination effluent ammonia concentration versus run number.

Based on the alkaline chlorination pilot results, a full scale treatment system could be expected to routinely meet it's NPDES permit limitations for all parameters except total cyanide. However, it should be remembered that the average influent cyanide value of the wastewater tested was approximately three times the BPT limit (30 mg/l) and cyanide values as high as nine times the BPT value were observed. It is unknown if BAT cyanide levels could be consistently met if better BPT treatment were provided. Values of cyanide-A exiting the pilot treatment system were typically <0.05 mg/l.

Dual Media Filtration Results

Dual media filtration tests were performed on the coke plant effluent as a

TABLE 2. COMPARISON OF SELECTED ALKALINE CHLORINATION RUN EFFLUENTS TO BAT LIMITATIONS

Run No.	ORP mv	NH_3, mg/l	CN_T, mg/l	O&G, mg/l	Phenol, mg/l	$S^=$, mg/l	SS, mg/l	SCN, mg/l
10	900	2	I	-	0.1	<0.2	7	2.3
11	960	2	0.2	-	0.2	<0.2	7	<1
12	960	3	0.7	12	0.4	<0.4	11	2.5
13	950	4	1.2	-	<0.01	<0.2	13	1.5
20	940	3	10.4	3	0.1	<0.2	10	15
22	940	2	6.1	-	0.2	<0.2	6	<1
BAT Limitations		13.4	0.33	13.4	0.27	0.4	27	200

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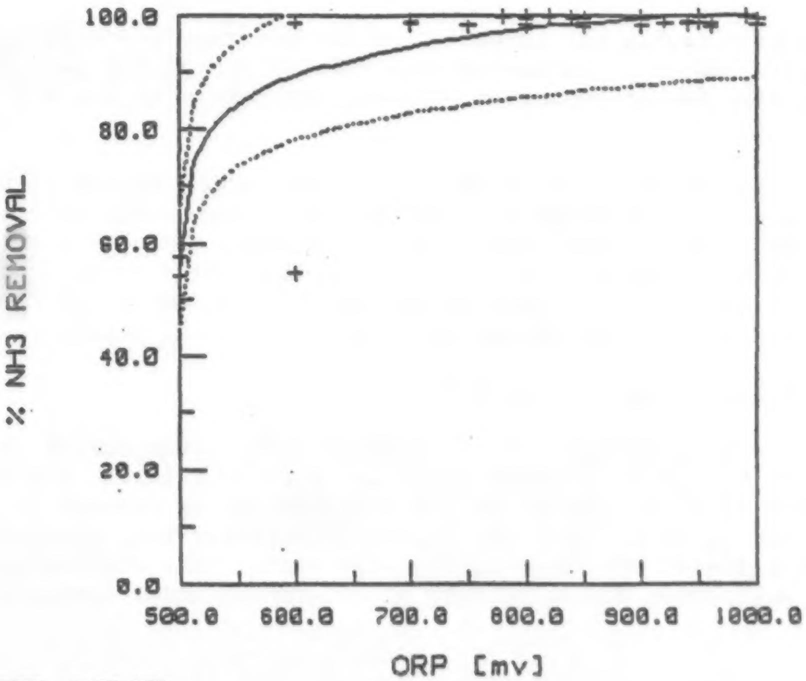

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INTERCEPT  = 33.103
SLOPE      = 17.117
Rsquared   = .719
CORRELATION= .848
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Figure 6. Ammonia removal versus ORP(mv) - alkaline chlorination.

polishing step from November, 1979 to January, 1980. Tests were conducted both with and without polymer.

Filtration results of the effluent without polymer are summarized in Table 3. Filtration removed significant quantities of suspended solids (71% removal). Table 3 also shows the average, maximum and minimum influent and effluent characteristics when chemically pretreated coke plant effluent was filtered with polymer as a coagulant aid. Overall removal of suspended solids (93% removal) was greatly improved with addition of the polymer at a dosage of 3 mg/l.

TABLE 3. DUAL MEDIA FILTRATION PILOT STUDY RESULTS

	Suspended Solids, mg/l No Polymer		Suspended Solids, mg/l Polymer Added	
	Inf.	Eff.	Inf.	Eff.
Average	51	11	71	3
Maximum	139	36	152	9
Minimum	7	2	10	1

Activated Carbon Results

The use of activated carbon was investigated to determine its effectiveness as a dechlorinating agent. The carbon will convert the excess chlorine produced by the alkaline chlorination process into chlorides and other harmless byproducts.

The average influent chlorine concentration to the carbon system during the study was 63.6 mg/l. The average chlorine removal rate across the carbon bed was 95 percent with a range from 83.9-100 percent. Removal efficiency decreased as volume processed increased. The carbon was also effective in reducing influent ammonia by 35 percent and TOC by 61 percent. Effluent phenol concentrations from the carbon were decreased by 73 percent.

Sodium Bisulfite Dechlorination Results

Sodium bisulfite was investigated as a dechlorinating agent during the pilot study. A plot of bisulfite:chlorine ratio and percent chlorine removal (Figure 7), shows that 100 percent of the chlorine can be removed at a bisulfite:chlorine ratio of 2:1. The figure illustrates that chlorine removal is a function of bisulfite to chlorine ratio. The studies were performed at a wastewater detention time of 30 minutes under complete mixing conditions.

Priority Pollutant Discussion (Physical/Chemical Test Site)

Priority pollutant analyses were performed on 63 samples of the coke plant wastewater plus blanks during the Phase I (alkaline chlorination-filtration-activated carbon) and Phase II (alkaline chlorination-sodium bisulfite dechlorination-filtration) investigations.

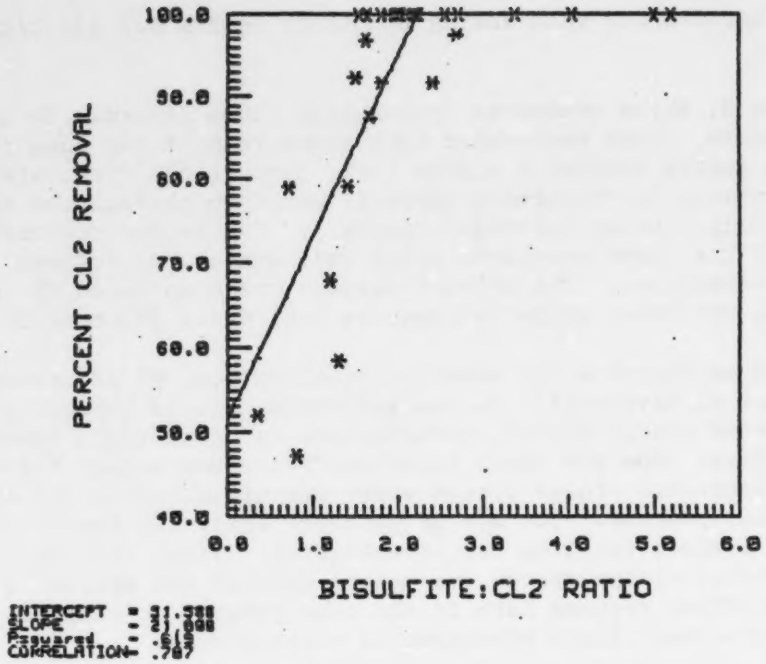

Figure 7. Plot of percent Cl_2 removal versus bisulfite:Cl_2 ratio.

Volatile Organics. Chlorination of the influent resulted in decreasing the concentration of benzene, acrylonitrile and toluene by approximately half. Chlorination increased chloroform concentrations from the 8 to 170 µg/l found in the raw influent to 3,700 - 22,000 µg/l in the chlorinated effluent. Dibromochloromethane, carbon tetrachloride, 1, 2 dichloroethane, chlorobenzene and bromoform were not detected in the influent samples; however, significant concentrations were found in the chlorinated effluent. Neither Phase 1 or Phase 2 treatment systems were completely effective in the removal of volatile organic priority pollutants. However, Phase 1 processes were superior, removing 10 to 100 times more volatile organics than Phase 2. Only negligible volatile organics removals were observed during Phase 2.

Semivolatile Organics. Phase 1 provided a more complete semivolatile organic priority pollutant removal than Phase 2. The Phase 1 operation removed all semivolatile organic priority pollutants to non-detectable limits. Phase 2 reduced all semivolatile organics to less than 100 µg/l except for naphthalene.

Metals. Phase 1 final effluent metals concentrations were very close to the initial raw influent levels. Similarly, priority pollutant metals were not removed in the Phase 2 operation.

EXPERIMENTAL RESULTS (BIOLOGICAL RESEARCH SITE)

General

The biological research work was performed at the Wheeling-Pittsburgh Steel Corporation's Steuvenville East coke plant from October, 1979 to February,

1980. The water application rate during the study period was 432 ℓ/kkg (104 gal./ton).

As shown in Figure 8, three treatment trains were investigated. In the first treatment train, plant wastewater from downstream of the coke plant cooling tower was passed through a mixing tank, through the first stage activated sludge system (carbonaceous removal) and then through the second stage activated sludge system (nitrogen removal). The second treatment train consisted of the first treatment train (bio-oxidation) followed by activated carbon adsorption. The third treatment train included the components of the first treatment train followed by dual media filtration.

The mix tank shown in Figure 8 was used for equalization, pH adjustment, dilution, and chemical dispersal. As the wastewater flowed through the first stage activated sludge system, carbonaceous material (BOD, Phenol, etc.) was removed. Effluent from the first stage clarifier was pumped through the second stage activated sludge system where ammonia nitrogen was oxidized by the nitrification process. The use of powdered activated carbon to remove toxics and improve settling was investigated. Final effluent from the second stage activated sludge system was passed through the activated carbon or dual media filtration systems late in the test program to complete the second and third treatment train arrangements respectively.

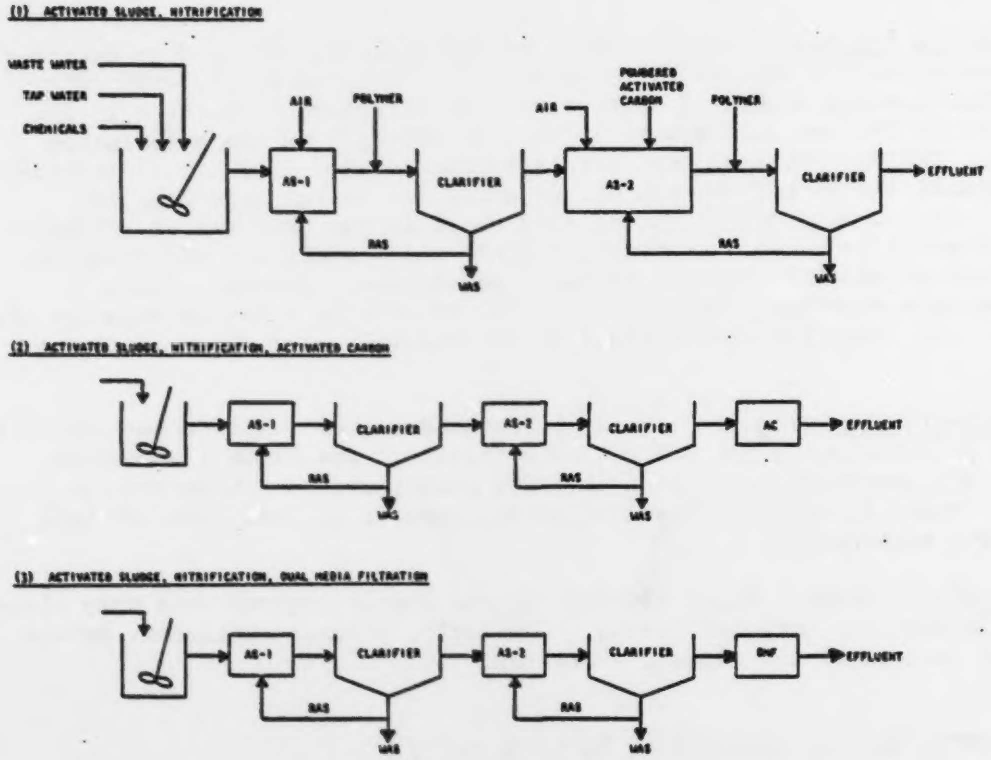

Figure 8. Process trains investigated for treatment of by-product coke plant wastewater.

Wastewater Treatment System

There are two primary process water streams associated with the by-product cokemaking operations at the plant investigated:

1. Benzol plant effluent.
2. Ammonia still excess liquor.

Strong ammonia liquor blowdown is stripped in the ammonia still by steam and caustic soda. Due to the steam and caustic soda injection, the volume of this stream increases and the temperature rises to ~94°C (200°F). Wastewater from the benzol plant is blended with the excess ammonia liquor from the ammonia still for dilution and cooling purposes. This mixture, of which about 25 percent is excess ammonia liquor, thereby is cooled to 44-67°C (112-152°F). After passing through an equalization tank and a cooling tower, the wastewater has lost sufficient heat to make it amenable to microorganism degradation. However, the waste still contains significant concentrations of pollutants toxic to biological life. Therefore, downstream from the cooling tower, coal yard runoff and dilution service water are added to the wastewater stream to make the waste acceptable to the plant's single stage activated sludge treatment system.

The coke plant's equalized wastewater was used as a source of feed to the pilot system during the study. Characteristics of this water are shown below in Table 4. BPT and BAT limits are also shown in the table for the plant investigated.

TABLE 4. FEEDWATER CHARACTERISTICS AND EFFLUENT LIMITATIONS FOR BIOLOGICAL RESEARCH SITE

Parameter	Diluted[1] feed	BPT[2] limit	BAT[2] limit
CN-T, mg/l	9.7	52	2
Phenol, mg/l	657	3.6	0.11
NH_3, mg/l	767	217	32
O&G, mg/l	17	26	20
SS, mg/l	70	223	86
Sulfide, mg/l	30.7	-	0.6
SCN, mg/l	451	-	1

[1] Diluted in the ratio of 3 parts coke plant equalized wastewater to 1 part service water.

[2] Dev. Doc., By-Product Cokemaking-EPA440/1-79/024a., Oct., 1979.

As shown above, the pilot system feedwater was well above BPT limits for phenol and ammonia during the test period.

Biological Treatment Results

First Stage Carbonaceous Removal System. The first stage pilot activated sludge system was effective in removing both BOD and phenol. The feedwater was pH adjusted and diluted (3 parts coke plant wastewater to 1 part service water) prior to pilot scale treatment. Phosphoric acid was also added.

Influent BOD ranged from 1,290 mg/l to 2,550 mg/l and averaged 1,800 mg/l. The BOD removal efficiency was typically 95% with a range from 60 percent to 99 percent. Good removals of phenol were also observed in the first stage system. Efficiency ranged from 90% to 100%. The average diluted feed phenol concentration was 657 mg/l, with a range from 440 mg/l to 920 mg/l. Removals of thiocyanate and TOC were also observed in the first stage treatment system.

Second Stage Nitrogen Removal System. The primary objective of the second stage bioxidation unit was to reduce influent concentrations of ammonia through the nitrification process. The pilot system feed ammonia during the study was quite variable, ranging from 293 mg/l to 2,553 mg/l after dilution. The average diluted feed ammonia concentration to the pilot units was 767 mg/l. The influent wastewater to the second stage was pH adjusted using sodium carbonate and sodium hydroxide. Powdered activated carbon was also added to reduce the effect of toxic shock loads and help weight the nitrified sludge. Polymer was also added to the second stage clarifier to minimize biomass losses over the weir.

Attempts to achieve a substantial population of nitrifiers were unsuccessful during the first six weeks of testing. Dilution to the second stage was initiated on December 1, 1979 to help reduce the wide fluctuations in feed ammonia concentration and therefore promote the growth of nitrifying bacteria. This had a positive effect on the microorganism population and nitrification began to take place in early January, 1980. Excellent ammonia removals were then consistently achieved for the duration of the project as shown in Figure 9. Test results for a period of time when nitrification was occurring are shown in Table 5.

TABLE 5. ANALYTICAL RESULTS FOR SELECTED TEST
PERIODS - NITRIFICATION SYSTEM

	SS (mg/l)		NH_3 (mg/l)		CN_T (mg/l)		CN_A (mg/l)		O&G (mg/l)		SCN (mg/l)		Phenol (mg/l)	
Date	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
1/16/80	47	56	206	17	2.0	I	<0.05	2.6	-	-	44	<1	-	-
1/18/80	34	66	228	8	3.6	I	<0.05	<0.05	3	11	4	<1	0.1	<0.1
1/21/80	26	61	171	2	5.6	I	<0.05	<0.05	2	8	3	<1	0.7	0.6
1/23/80	27	51	160	1	8.3	I	<0.05	<0.05	-	-	2	<1	-	-
1/25/80	41	59	156	3	9.3	I	<0.05	<0.05	4	6	1	<1	0.2	0.1
1/28/80	57	93	234	6	13.3	I	<0.05	<0.05	7	3	2	<1	0.1	<0.1

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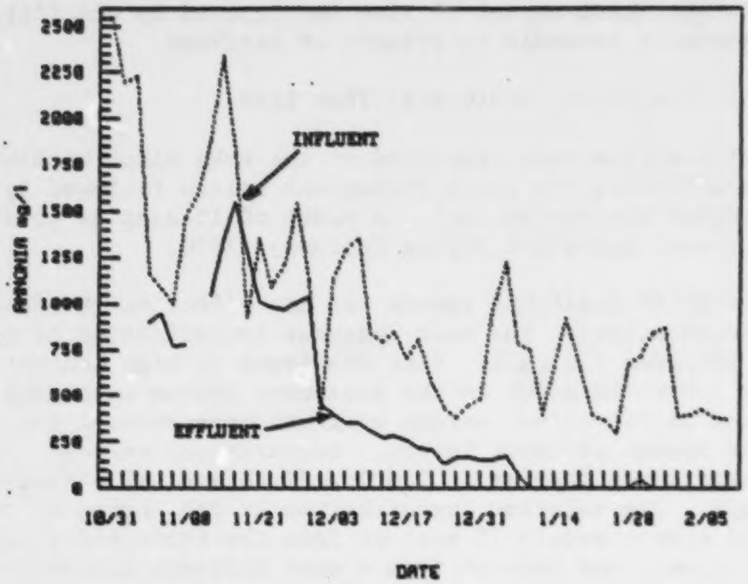

Figure 9. Influent ammonia versus AS-II effluent ammonia.

By comparing the Table 5 analytical results with the BAT limits shown in Table 4, it is apparent that BAT guidelines could be met for all parameters.

Activated Carbon Results. The results of the biological test site activated carbon study determined that carbon was effective in removing TOC (53% removal), color (60% removal), BOD (40%) and SCN (79% removal) from the second stage activated sludge effluent. There were also minor removals of phenol, oil and grease and TKN.

Dual Media Filtration Results. Dual media filtration tests were also performed on the nitrified effluent. Runs were conducted at filtration rates of 122, 204, 326 and 407 ℓ/min/m² (3, 5, 8 and 10 gpm/ft²). During the study, influent suspended solids averaged 190 mg/l. Removal efficiency ranged from 17 to 64 percent.

During one of the dual media filtration runs, samples of influent, effluent, and backwash were collected for metals analysis. The metals analysis data are summarized in Table 6.

TABLE 6. DUAL MEDIA FILTRATION HEAVY METALS REMOVAL

Sample Point	Heavy Metal Concentration, mg/l						
	Cu	Cd	Pb	Zn	As	Se	Sb
Influent	0.06	0.03	<0.1	2.4	<0.0005	0.56	<0.05
Effluent	0.05	0.03	<0.1	0.9	<0.0005	0.42	<0.05
Backwash	0.86	0.13	0.20	30.0	<0.0005	2.33	<0.05

As seen in Table 6, copper, cadmium and selenium were removed in trace amounts, while a significant amount of zinc was removed by the filter. There were no measurable removals or arsenic or antimony.

Priority Pollutant Discussion (Biological Test Site)

Priority pollutant analyses were performed on the coke plant wastewater treated in the experimental two stage biological system followed by the pilot activated carbon adsorption unit. A total of 13 samples plus appropriate blanks were collected during February, 1980.

Metals. The pilot treatment system was not effective in reducing influent zinc concentrations. The mean influent concentration of zinc was 443 µg/l and the effluent 400 µg/l. Zinc was found in high concentration (630 µg/l) in the raw water added to the treatment system as makeup water. Zinc concentrations in the carbon column effluent were reduced threefold from the activated sludge effluent levels. Selenium was reduced by 77% from a mean influent concentration of 1,370 µg/l to a final effluent concentration of 320 µg/l. The selenium concentration in the carbon column effluent decreased approximately 25 percent from the activated sludge effluent level. Arsenic was reduced from a mean influent concentration of 360 µg/l to an effluent concentration of 99 µg/l. Influent silver concentration was 18 µg/l compared to an effluent level of 12 µg/l. All the other priority pollutant metals were removed to concentration levels close to or below detection limits.

Volatile Organics. The treatment process was effective in removing all volatile organic priority pollutants. Toluene was reduced from a mean influent concentration of 607 µg/l to a final effluent of less than 10 µg/l (on two of the three sampling dates). While the activated sludge system influent contained 6,100 µg/l to 9,800 µg/l of benzene, no benzene was detected in the activated sludge or the final carbon column effluents. All other volatile organic compounds in the activated sludge and carbon column effluents were generally below the detection limits.

Base/Neutral Extractable Organics. The treatment process was effective in reducing all monitored base/neutral extractable organics. The concentration of all nine of the base/neutral compounds found in the influent was reduced through the treatment process to less than 10 µg/l in the activated sludge final effluent.

Acid Extractable Organics. All acid extractable organic compounds monitored were effectively removed by the treatment system. For example, the system influent contained a mean concentration of 62 mg/l phenol. Phenol was reduced by the treatment process to less than the detection limit in the final effluent. All other acid extractable organic compounds in the final effluent were below the detection limit.

SUMMARY AND CONCLUSIONS

Physical-Chemical Test Site. Two physical-chemical treatment trains were investigated. Train 1 consisted of alkaline chlorination, filtration and activated carbon. Train 2 consisted of alkaline chlorination, filtration and sodium bisulfite dechlorination.

1. The results of the pilot program indicated that alkaline chlorination was effective in reducing influent concentrations of ammonia, oil and grease, phenol, sulfide, suspended solids and thiocyanate to below future BAT levels. The presence of complexing agents in the coke plant effluent prevented complete oxidation of the cyanide by chlorine and as a result, BAT cyanide-T values could not be consistently met.

2. Filtration provided effective polishing of the alkaline chlorinated coke plant effluent, removing 71 percent of the influent suspended solids. Suspended solids removal could be increased to 93 percent with the addition of 3 mg/l polymer.

3. Activated carbon and sodium bisulfite were investigated as dechlorinating agents. Activated carbon was found to consistently remove 95 percent of the incoming total chlorine. Sodium bisulfite provided 100 percent chlorine removal at a bisulfite:chlorine ratio of at least 2:1.

4. During the pilot study, 63 samples were analyzed for priority pollutants. The results concluded that the physical/chemical treatment trains investigated created several volatile organic priority pollutants. Phase I technologies removed 73% of the volatile organic priority pollutants to non-detectable limits; Phase 2 technologies were effective in treating only 17% of incoming volatile organic toxics to non-detectable levels. Semivolatile organics were all effectively reduced for Train 1. Train 2 also reduced all semivolatile organics to less than 100 µg/l except for naphthalene. The physical/chemical treatment trains removed only negligible concentrations of metals.

Biological Test Site. A pilot scale two stage activated sludge unit was investigated for removing coke plant wastewater contaminants to below BAT values. Filtration and activated carbon were also studied as polishing steps.

1. The first stage activated sludge unit was capable of removing 95 percent of the influent BOD and from 90-100 percent of the incoming phenol. Thiocyanate and TOC reductions were also achieved.

2. Influent ammonia to the second stage activated sludge system was quite variable, ranging from 293 mg/l to 2,553 mg/l. It was necessary to dilute the first stage activated sludge effluent to maintain a consistent feed ammonia strength before nitrification could be achieved. After a sufficient population of nitrifiers were in the system, ammonia reductions of >97 percent were consistently achieved. Suspended solids, oil and grease, thiocyanate and phenol were also reduced to below BAT levels.

3. Activated carbon, when used as a polishing step for the nitrified effluent, was capable of removing 53 percent of the influent TOC, 60 percent of the color, 40 percent of the BOD and 79 percent of the remaining thiocyanate.

4. Dual media filtration was found to remove about 50 percent of the suspended solids present in the second stage activated sludge nitrified effluent.

5. Priority pollutant analyses were performed on 13 samples taken from various points in the treatment system. All priority pollutant metals were reduced to less than 100 µg/l except for selenium and zinc. The biological treatment train was efficient in removing all volatile organics, base/neutral extractable organics and acid extractable organics to non-detectable levels.

ACKNOWLEDGEMENTS

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The information contained in this paper is part of a draft final report being prepared for the U.S. Environmental Protection Agency. Modifications to the enclosed material prior to publication of the final report are probable.

SINGLE STAGE NITRIFICATION OF COKE PLANT WASTEWATER

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ABSTRACT

A laboratory scale study of single stage phenol oxidation-nitrification activated sludge treatment of coke plant wastewater was conducted. The objectives of the study were to determine:

- the operating conditions at which a treated effluent would contain an ammonia concentration of 10 mg/l or less,
- the effects of sudden changes in loadings of certain wastewater constituents on the biological process,
- the effects of the process on priority organic pollutants, and
- means of enhancing the biological process.

In this study, eight test reactors were used; the feed to these reactors was undiluted ammonia still waste which was ammended to a constant composition of ammonia, phenol and thiocyanate.

The results of the study show that the single stage phenol oxidation-nitrification process can produce high degrees of treatment for ammonia, free cyanide, phenol, thiocyanate and sulfide but it was ineffective in treating complex cyanide. This process is also effective in controlling priority organic pollutants found in coke plant wastewater. Sudden changes in the reactor loadings of conventional pollutant constituents resulted in neither toxic nor prolonged inhibitory effects. However, the process was sensitive in responding to abrupt changes in feed composition and reactor composition. These responses to changes should be tested on a full scale operation such that the true impact of normal coke plant operations could be assessed. The preliminary evaluation of activated carbon addition, carbonate addition and commercial mutant bacteria addition as means of enhancing (increasing the rate of nitrification) were inconclusive.

This study was conducted in fulfillment of an EPA Grant (No. R806234-01-2) which provided partial funding for this program.

SINGLE STAGE NITRIFICATION OF COKE PLANT WASTEWATER

INTRODUCTION

The Environmental Protection Agency's proposed "Best Available Technology Economically Available," BAT, effluent guidelines for by-product coke plant wastewaters may include: ammonia, cyanide (total), oil and grease, phenolic compounds, sulfides, thiocyanates and priority pollutants. Alternative technologies for achieving compliance with the proposed effluent guidelines are (a) physical chemical technology and (b) biological treatment. The proposed BAT biological technology suggests a multi-stage biological treatment system which includes a phenol removal reactor, cyanide-ammonia oxidation reactor followed by a nitrate reduction reactor and a final step aeration for the reoxidation of sulfide. Figure 1 presents a flow diagram of the proposed BAT treatment system showing a free/fixed leg ammonia still pretreatment stage. This report deals with a single reactor alternative for phenol oxidation/nitrification.

Previously, National Steel conducted a preliminary examination of a single stage biological reactor to determine the feasibility of this technology to produce compliance with proposed BAT limitations. Although the evaluation had not progressed sufficiently to conclude whether the process was a viable treatment alternative, the results were sufficiently encouraging to warrant further examination. The preliminary testing with a single stage pilot reactor, treating coke plant ammonia still waste showed that both phenol oxidation and nitrification could be achieved in single reactor system. However, too often periods of sustained effective operation were interrupted by unidentified episodes which completely disrupted the nitrification process; subsequent start-up after an interruption required an extended period of reacclimation. These extended periods were as long as seven weeks.

Undoubtedly, those unidentified disruptive episodes are causes for concern in any decision to apply this technology on a full scale and in many respects they reflect the level of understanding of this technology. Consequently, this program was initiated. The objectives of the program were:

(1) To determine the operating conditions necessary to produce an effluent with an ammonia concentration of 10 mg/l or less and to determine the corresponding concentration of the other conventional pollutants,

(2) To determine the effects of certain constituent compounds in coke plant wastewater on the performance of the single stage phenol oxidation/nitrification process,

(3) To conduct a preliminary examination of methods for enhancing the operation/performance of the single stage phenol oxidation/nitrification process,

(4) To determine the effects of the single stage phenol oxidation/nitrification process on priority organic pollutants in coke plant wastewaters, and

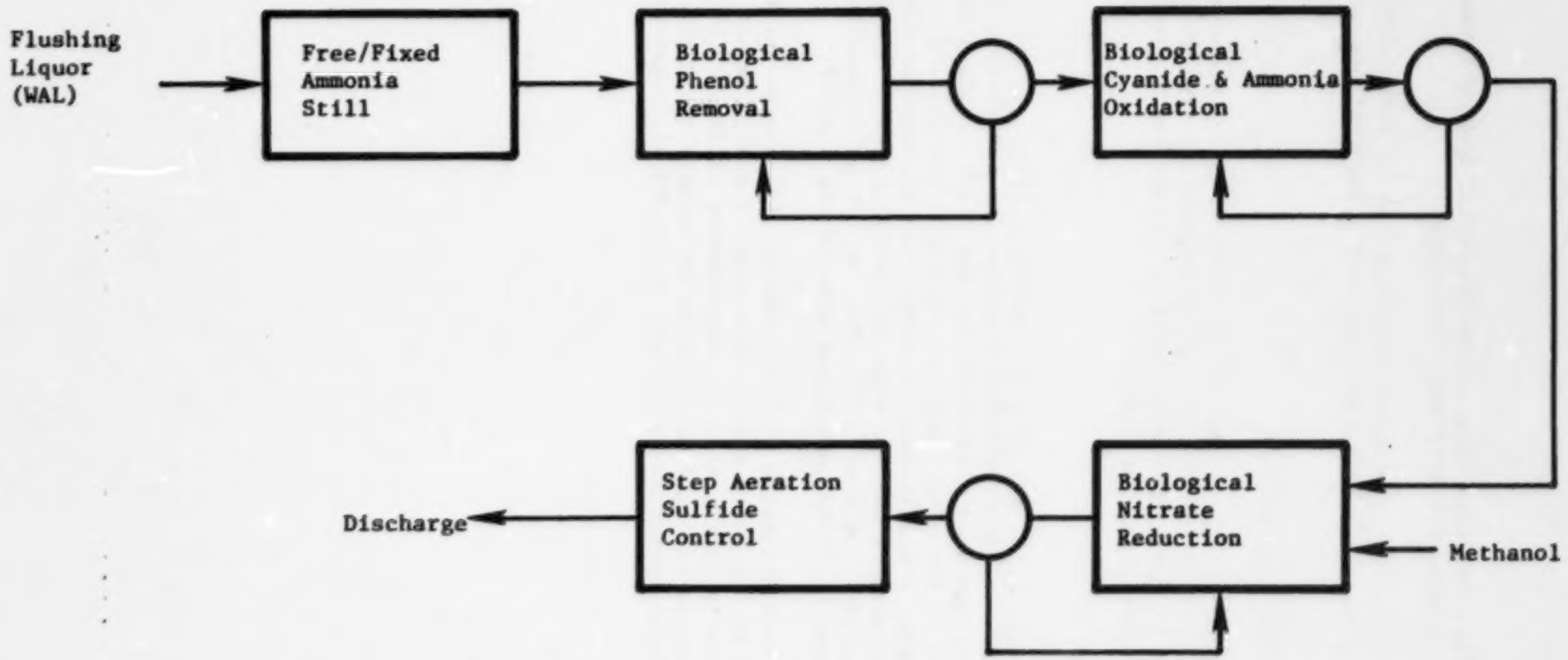


Figure 1. Flow Diagram of Proposed BAT Treatment System for By-Product Coke Plant Wastewaters.

(5) To develop a better understanding of the operation and performance of the single stage phenol oxidation/nitrification process.

The program was essentially a laboratory investigation in which actual coke plant wastewater was examined. This report presents the findings of this program.

INVESTIGATIVE FACILITIES AND PROTOCOL

The experimental program was conducted at the National Steel Corporation Research Center. Facilities for the biological wastewater treatment experiments included: 1) a sludge bank reactor unit; 2) eight bench scale reactor units and 3) support analytical facilities.

Sludge Bank Unit (SBR)

The sludge bank unit was a 160 gallon pilot reactor, Figure 2, which served as a source of readily available acclimated sludge for the experimental program. This pilot unit was used previously for the single stage biological experiments which led to the study program. Although the unit was composed of two discrete vessels, a single reactor effect was achieved by the common heads between the two vessels and the high recirculatory rate. This reactor has been in operation since October 1977. Feed to the pilot unit came from the Weirton Steel Brown's Island coke plant ammonia still (ASW).

Because of the long term operation of this reactor, the sludge in the reactor was fully acclimated to the wastewater. This readily available source of acclimated sludge greatly facilitated the experiments which were conducted by circumventing the long operating time required for sludge acclimation. Thus, the experiments could be conducted to satisfy the hydraulic requirements for steady state.

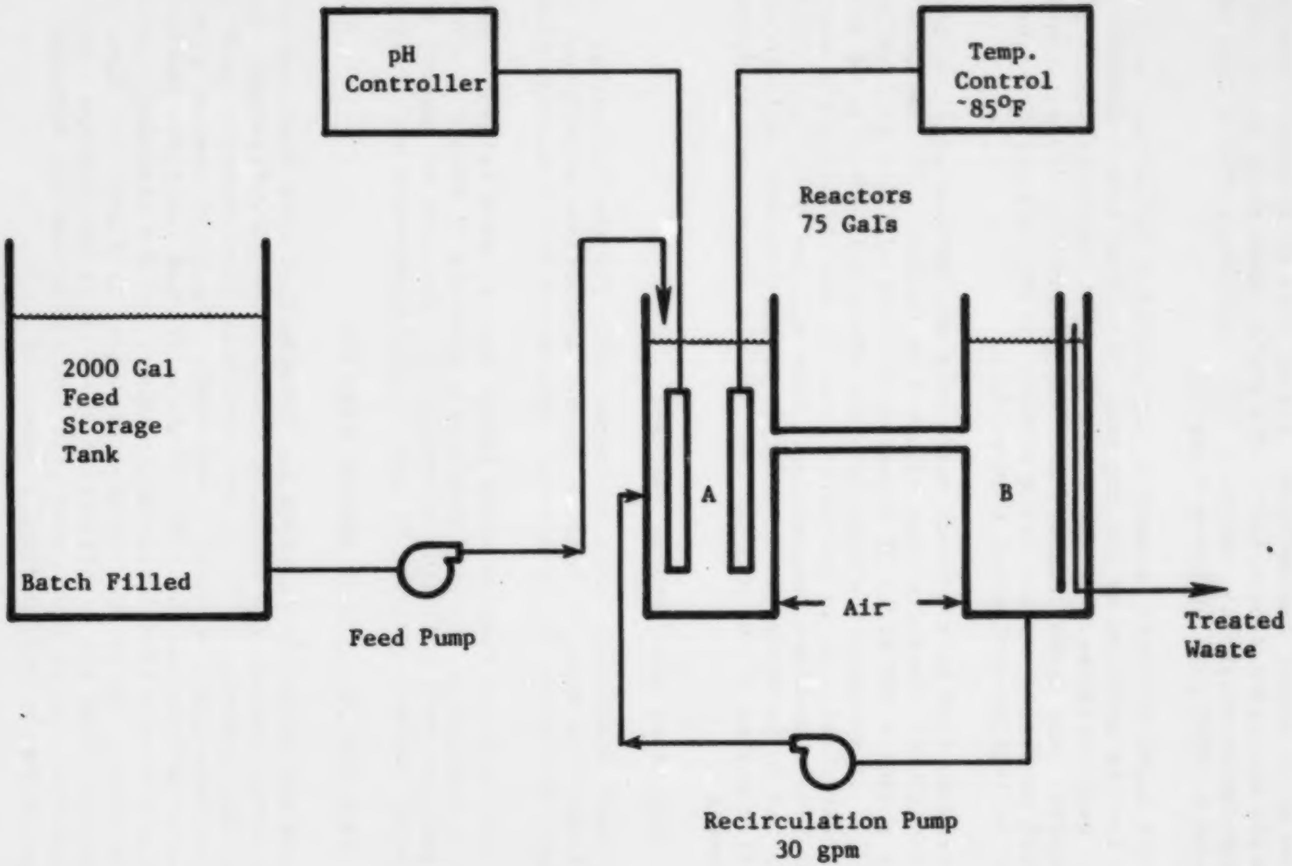


Figure 2. Sludge Bank Reactor Unit.

Bench Scale Reactors

The bench scale reactors were all activated sludge type systems with a 31 liter aeration chamber and integral clarifier. Each unit was equipped with its own feed system which enabled independent operation relative to operating condition or feedwater composition. Figure 3 is an isometric diagram of a bench scale activated sludge unit. The eight bench scale units were housed in a temperature controlled cabinet. The temperature within this cabinet was maintained at 85°F plus or minus 2 degrees.

One of the eight reactors, number 2, was operated exclusively as a control reactor for the duration of the program. The other seven reactors were used to study test variables. Often, a specific test condition was examined in two reactors. All eight reactors were continuously monitored. When a specific test condition was not being examined in any reactor that reactor was used for collecting additional control data.

The wastewater feed to the bench scale unit was ammonia still waste with the major constituent concentrations adjusted as follows: 1) ammonia - (NH_3) = 150 mg/l, 2) phenol = 500 mg/l, 3) thiocyanate = 300 mg/l and 4) alkalinity = 1060 mg/l. In subsequent discussions the above ASW feed will be referred to as a standard feed. It is recognized that in real practice the wastewater will not have a constant composition. However, the variability in feed composition had to be minimized in order to better evaluate variable effects. In specific phases of the program the feed was changed to meet desired requirements.

Reactor Monitoring and Chemical Analyses

All the bench scale units were monitored daily for the following: 1) feed and effluent flow rate, 2) reactor pH with appropriate adjustments when necessary, 3) reactor DO, 4) reactor temperature and 5) reactor sludge volume.

Appropriate feed and reactor mixed liquor samples were taken for analyses as per Standard Methods. Table 1 presents a schedule of sample analysis. Additional analyses were conducted as necessary. Two sets of samples were taken for priority organic analyses by gas chromatography-mass spectrograph.

SINGLE STAGE CONTINUOUS FLOW REACTOR KINETICS

Wong-Chong and Caruso(1) examined the treatment of coke plant wastewater in a single stage reactor for phenol degradation and nitrification. Their study examined the treatment in batch and continuous flow reactors; both synthetic and actual coke plant wastewater were used. The batch reactor experiments provided information on the order of the different reactions involved, some insight into interactions which might occur, and the sequence in which the reactions occur. These observations are shown in Figure 4. These observations indicate that the nitrification reaction is the process controlling step and the reaction is of zero order with respect to ammonia nitrogen. Thus, the reaction can be mathematically described as

$$\frac{d\Sigma N}{dt} = k_A/\mathrm{MLSS} \qquad (1)$$

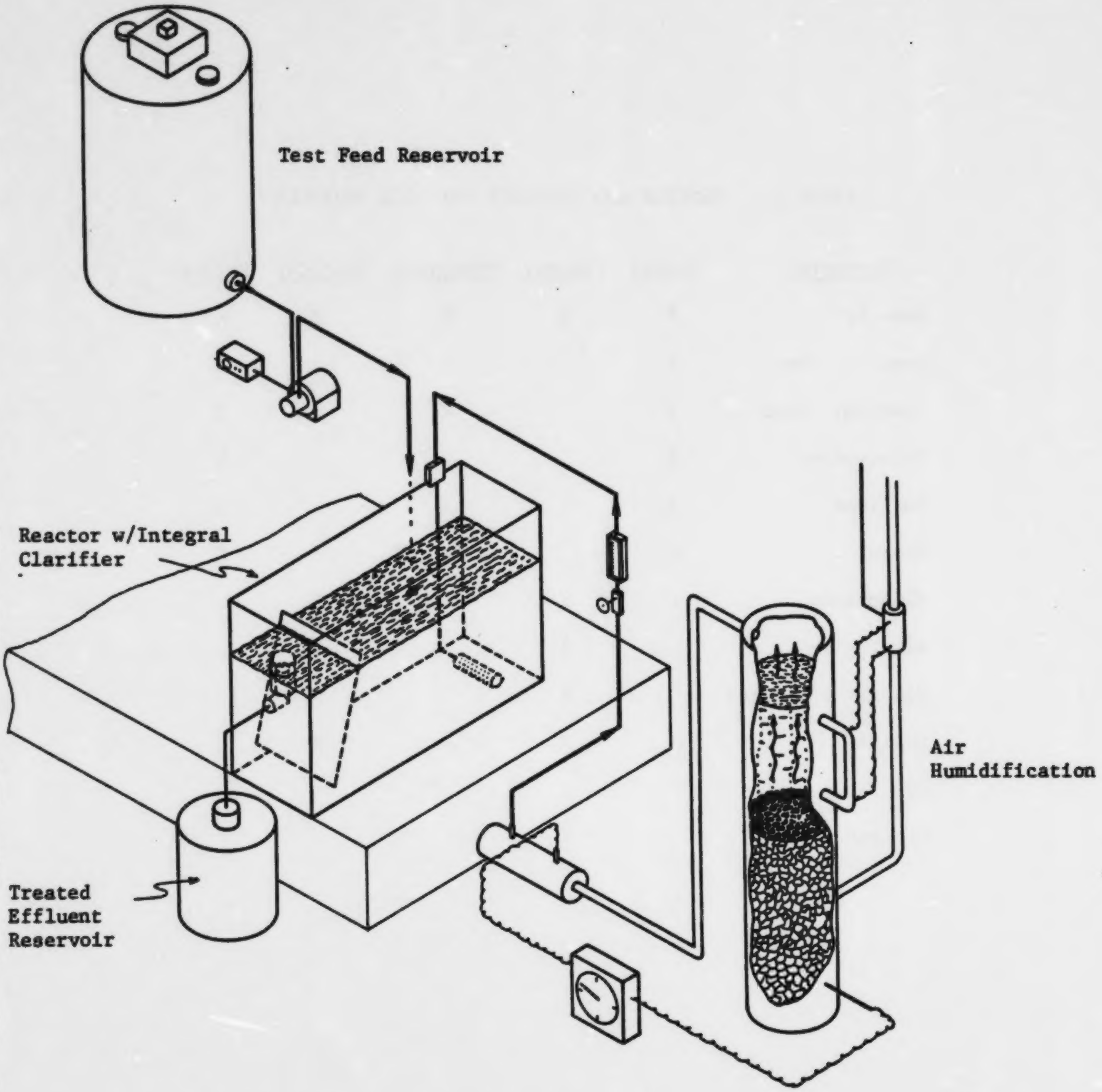


Figure 3. Isometric Diagram of Bench-Scale Activated Sludge Unit

Table 1. REACTOR AND EFFLUENT ANALYSIS SCHEDULE

Parameter	Monday	Tuesday	Wednesday	Thursday	Friday
Ammonia	X	X	X	X	X
Cyanide, Free	X		X		X
Cyanide, Total	X		X		X
Thiocyanate	X		X		X
Sulfides	X		X		X
Phenol	X		X		X
Phosphates		X		X	
Alkalinity		X		X	
Nitrite & Nitrate		X		X	
Solids		X		X	
COD		X			
Oil and Grease		X			

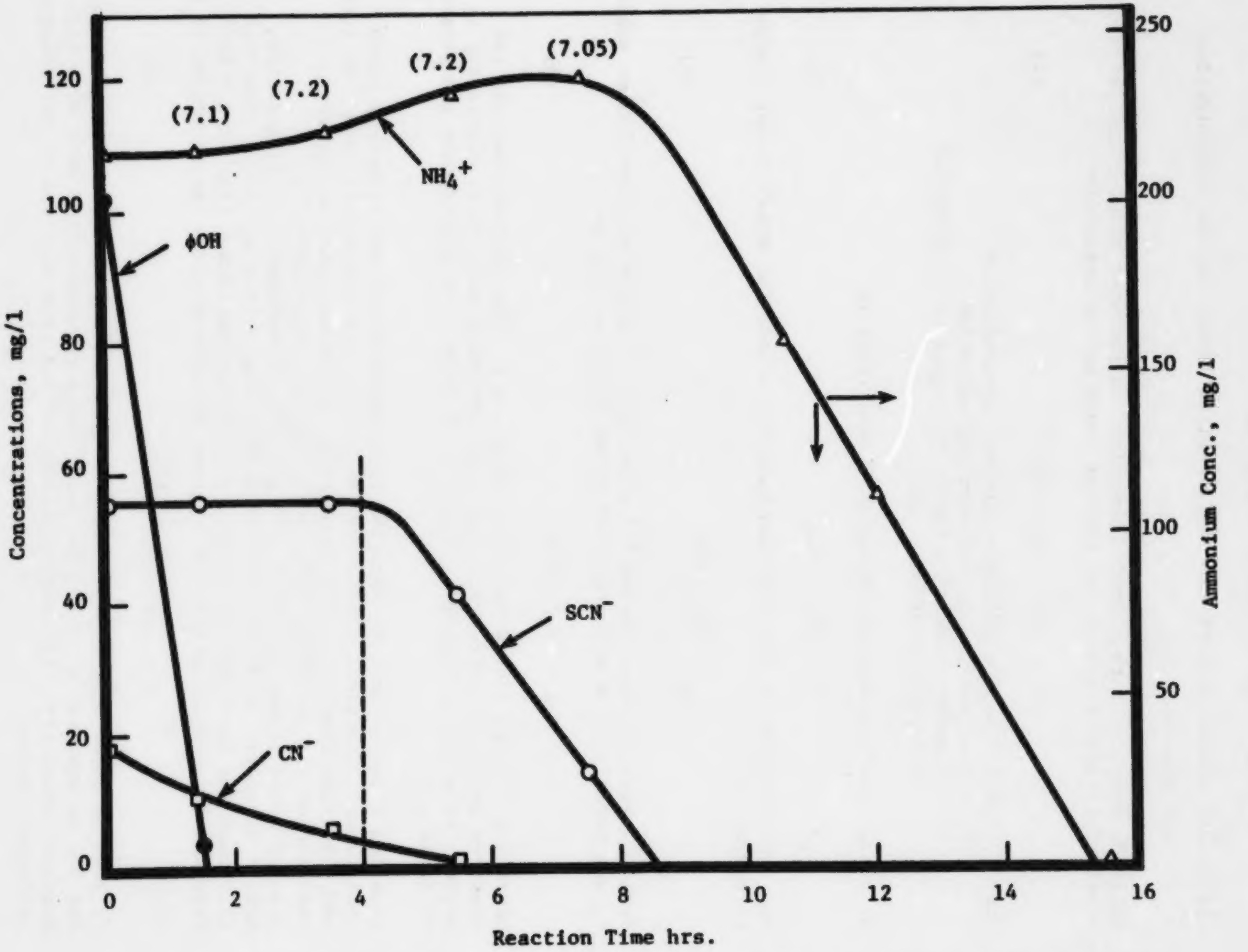


Figure 4. Reaction Sequence for Ammonia, Cyanide, Phenol and Thiocyanate in a Batch Reactor.

where ΣN = concentration of oxidizable nitrogen.
= $NH_4^+ - N + 0.54\ CN_F^- + 0.24\ SCN^-$

$k_A/MLSS$ = oxidation rate for a given mixed liquor solids concentration

t = reaction time

Applying Equation 1 to a continuous flow, batch mixed reactor and performing a material balance around the reactor produces the expression

$$\Sigma N = \Sigma N_i - \tau k_A - A_1 e^{-t/\tau} \qquad (2)$$

where ΣN = effluent oxidizable nitrogen concentration
ΣN_i = feed oxidizable nitrogen concentration
A_1 = boundary condition factor (constant of integration)
τ = hydraulic residence time

at steady state condition, Equation 2 simplifies to

$$\Sigma N = \Sigma N_i - \tau k_A \qquad (3)$$

and from Equation 3, the reaction rate for a specific mixed liquor sludge can be expressed

$$k_A = \frac{\Sigma N_i - \Sigma N}{\tau} \qquad (4)$$

From the previous observations(1) with various levels of mixed liquor solids, k_A was correlated as a function of mixed liquor solids as

$$k = 15.2\ (TVS) \qquad (5)$$

where TVS = mixed liquid volatile solids, g/l. The control reactors had measured oxidation rates which had good agreement with those previously reported, as shown in Figure 5. Details of these test experiments are presented in Table 2.

Equation 2 can be used to describe both steady state and transient state operations. Transient conditions can result from changes in feed flow rates and substrate loadings. This occurrence is demonstrated in Figure 6. The reactor was operating under the following conditions: 1) reactor mixed liquor solids = 4.20 g/l TVS, 2) hydraulic residence time, HRT, = 3.9 days and 3) nitrogen oxidation rate = 55.6 mg/l/day. The feed flow rate was increased to produce a hydraulic residence time of 2.2 days. From the above information, the reactor ΣN concentration can be predicted by

$$N = 104 - 96e^{-0.45T} \qquad (6)$$

It must be noted that a major fraction of the residual oxidizable nitrogen was due to ammonia, although the thiocyanate concentrations were very high. However, these high thiocyanate concentrations were well within the range of predicted values.

Figure 5. Agreement Between the Oxidation Rates from Control Reactors of this Program and that Previously Reported.

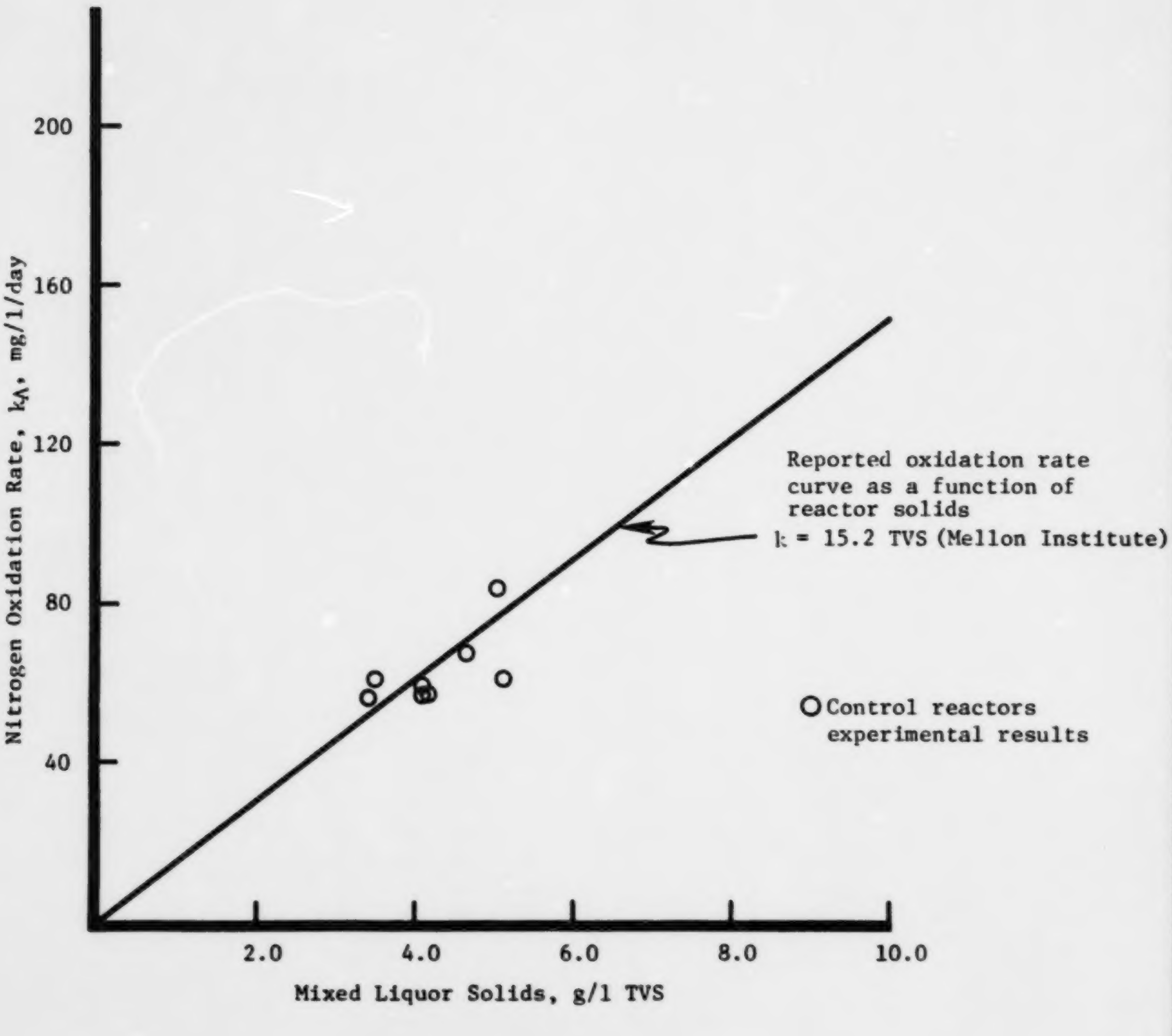


Table 2. DETAILS OF THE OPERATION OF CONTROL REACTORS

Feed Composition

Phenol = 500 mg/l NH_3 = 150 mg/l
CN_F = <0.1 mg/l   SCN = 300 mg/l
ΣN = 225 mg/l

	Reactor Operating Conditions						Average Effluent Composition[d]			
Reactor	pH	τ days	SRT[a] days	k mg/l/day	MLTVS g/l	MLSS g/l	NH_3	SCN mg/l	CNF	φOH μg/l
1	6.5-7.6	3.7	192	57.5	4.24	4.05	11±18	5±6	<0.1	20±20
2	7.0-7.5	3.5	250	60.9	5.10	5.17	9±16	11±22	<0.1	17±16
3	7.2-7.7	3.3	174	67.0	4.65	4.58	4±3	11±10	<0.1	17±11
3A	6.9-7.6	3.7	177	56.2	4.14	3.91	12±22	13±19	<0.1	25±28
4[b]	7.0-7.6	3.8	96	59.9	3.47	3.03	7±8	9±10	<0.1	31±47
6	7.1-7.6	2.7	153	83.0	5.05	5.10	14±25	11±19	<0.1	22±26
7	7.1-7.4	3.9	156	55.6	4.20	3.99	7±10	6±5	<0.1	68±90
7A[c]	7.1-7.6	5.0	282	54.9	3.43	2.98	3±2	29±46	<0.1	79±58

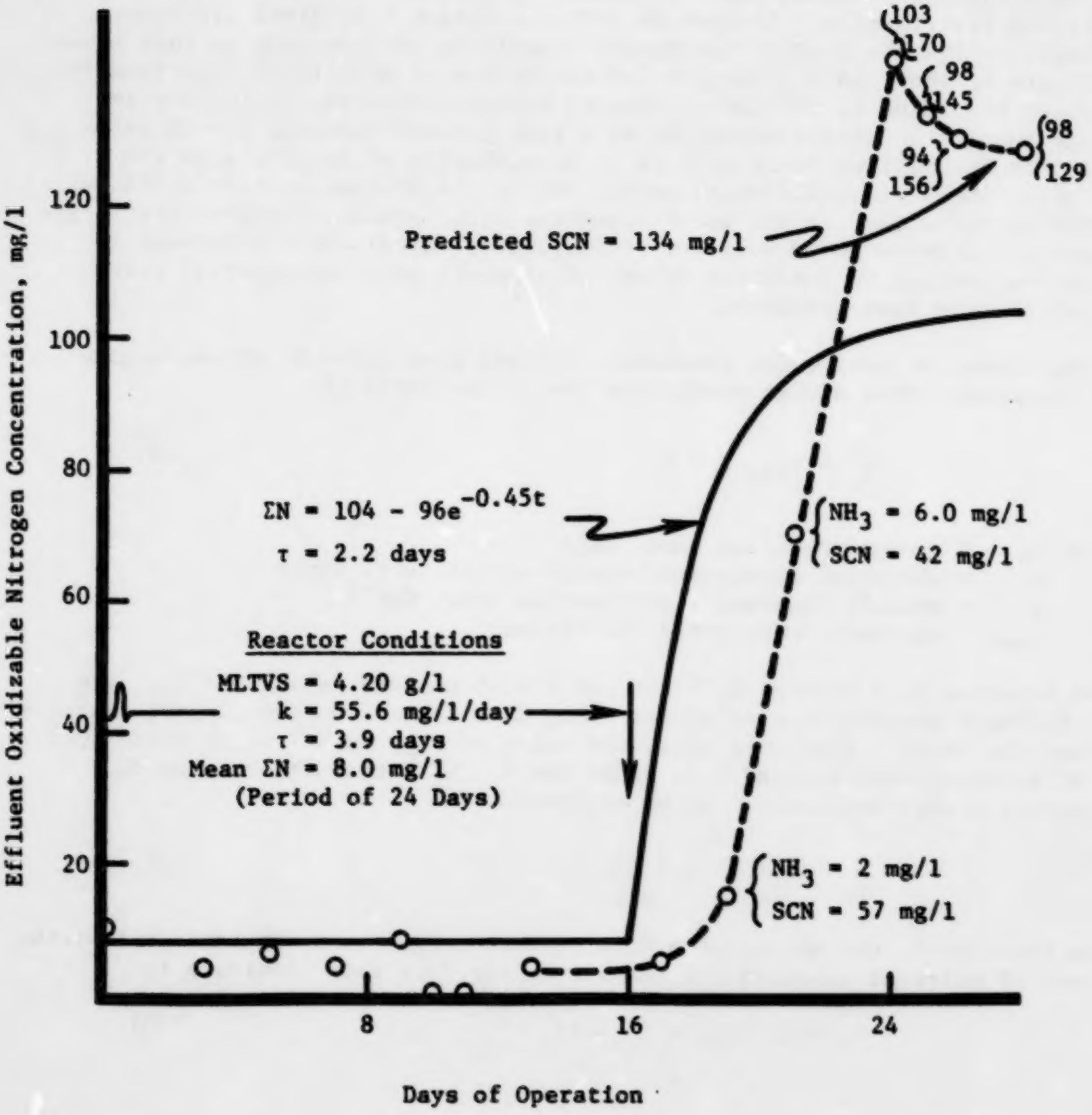
(a) Basis - suspended solids

(b) Feed contains 350 mg/l SCN

(c) Feed contains 210 mg/l NH_3

(d) Negative values observed due to variability in the actual numbers.

Figure 6. Prediction of Transient Conditions Using Equation 2.



The thiocyanate concentrations can be predicted by an equation similar to Equation 2, where the thiocyanate concentrations are substituted for nitrogen. Thus, for the situation shown in Figure 6, the degradation rate k_{SCN} is 75.4 mg/l/day and

$$S = S_i - 75.4\,\tau - Be^{-T/\tau} \qquad (7)$$

$$S = 134 - 28\,e^{-0.45T} \qquad (7A)$$

From Equation 7A, the new steady state concentration of thiocyanate would be 134 mg/l which compares well with those observed as shown in Figure 6.

In comparing the predicted with those of the observed, one notices a marked difference, especially in the early stages of the transition period. At best the mathematically formulations presented will provide an estimate of effects resulting from changes. It must be recognized that biological treatment systems are dynamic systems and during transition periods such as that shown in Figure 6, there is a potential for the number of nitrifying organisms to increase resulting in the lower observed values. However, if the imposed change results in events occurring at a rate greater than the growth rates of the organisms then there will be an accumulation of materials in the reactor. These materials which accumulate in the reactor in turn could exert an inhibitory effect on the micro-organisms once certain tolerance levels are exceeded. Alteration of activity by inhibitory materials could result in severe reductions in oxidation rates. The result would be observed rate values greater than predicted.

In the course of biological treatment, certain quantities of excess sludge are produced. This sludge production can be predicted by

$$\frac{1}{\theta_c} = y_{max}\,U - b \qquad (8)$$

where θ_c = sludge retention time, days
b = microbial maintenance energy coefficient, day^{-1}
U = specific substrate utilization rate, day^{-1}
y_{max} = maximum sludge yield coefficient

From Equation 8, a plot of θ_c^{-1} against U will produce values for y_{max} and b. Figure 7 presents a plot of operating data taken from the control reactors during the study. From this plot, the value of y_{max} is 0.7 mg SS formed per mg of nitrogen oxidized and b is 0.004 day^{-1}. With this information the potential sludge production can be estimated from

$$\frac{1}{y_e} = \frac{1}{y_{max}} + \frac{b\,\theta_c}{y_{max}} \qquad (9)$$

From Equation 9, the amount of sludge produced, S_p, can be determined from the amount of nitrogen oxidized and the wastewater flow rate according to

$$S_p = Q\,(\Sigma N_{in} - \Sigma N_{out})\,y_e \qquad (10)$$

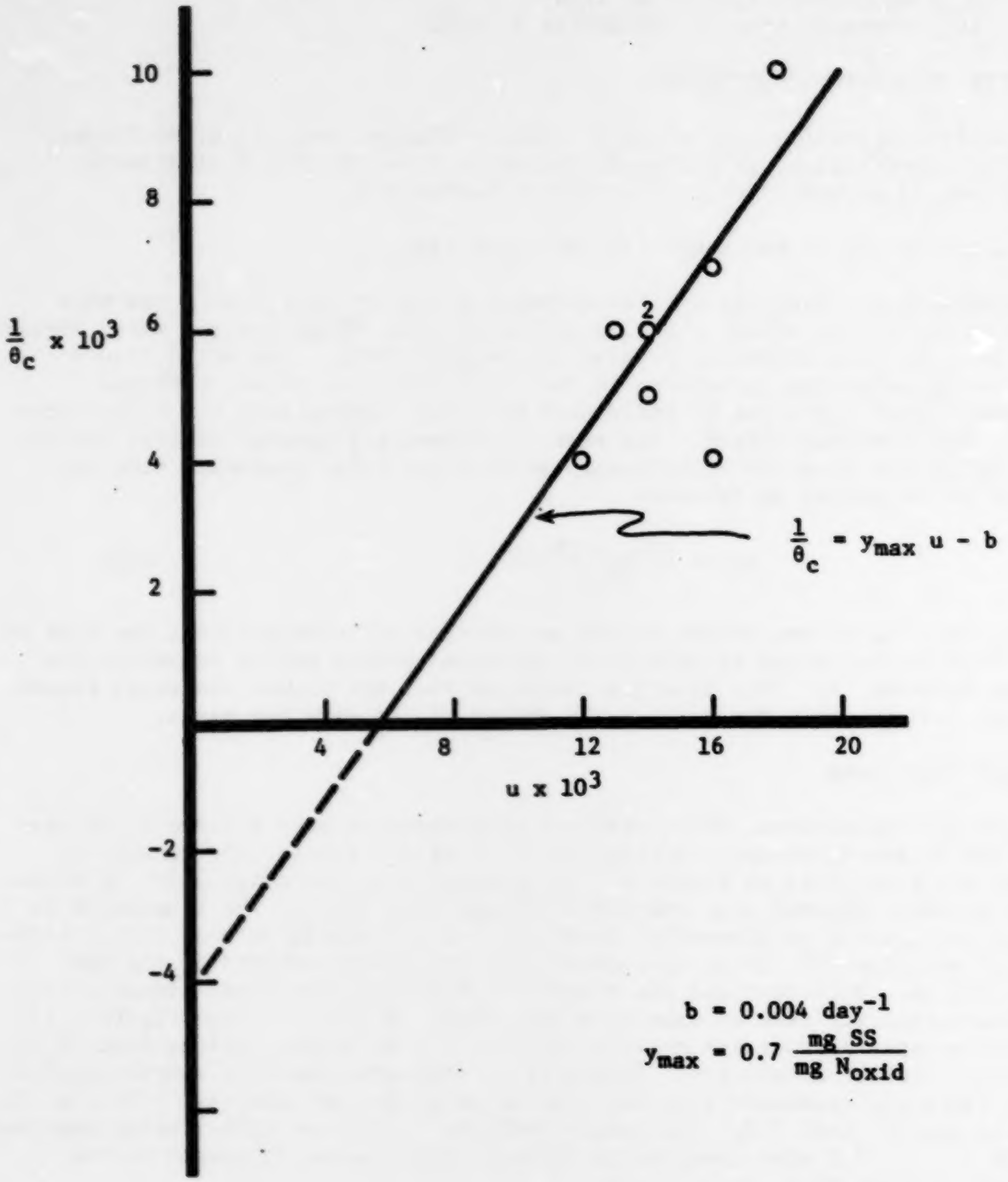


Figure 7. Sludge Production in the Single-Stage Phenol-Nitrification Process for Coke Plant Wastewaters.

where S_p = sludge production rate, mg SS/l/day
Q = wastewater flow rate, l/day
ΣN = concentration of oxidizable N, mg/l

EFFECTS OF REACTOR CONDITIONS

The reactor operating conditions of primary concern are: 1) mixed liquor solids concentration, 2) hydraulic residence time, 3) pH and alkalinity, 4) dissolved oxygen concentration and 5) temperature.

Mixed Liquor Solids and Hydraulic Residence Time

In designing a biological treatment system there are essentially two main factors which will affect the size of the system. These are the mixed liquor solids concentration and the hydraulic residence time. The mixed liquor solids concentration is related to the reactions rates shown in Figure 5. However, these rates can be influenced by other factors such as pH, temperature, and dissolved oxygen. The reaction kinetics presented earlier can be manipulated to show the relationship between hydraulic residence time and mixed liquor solids as follows:

$$TVS = \frac{\Sigma N_{in} - \Sigma N_{out}}{15.2\ \tau} \qquad (11)$$

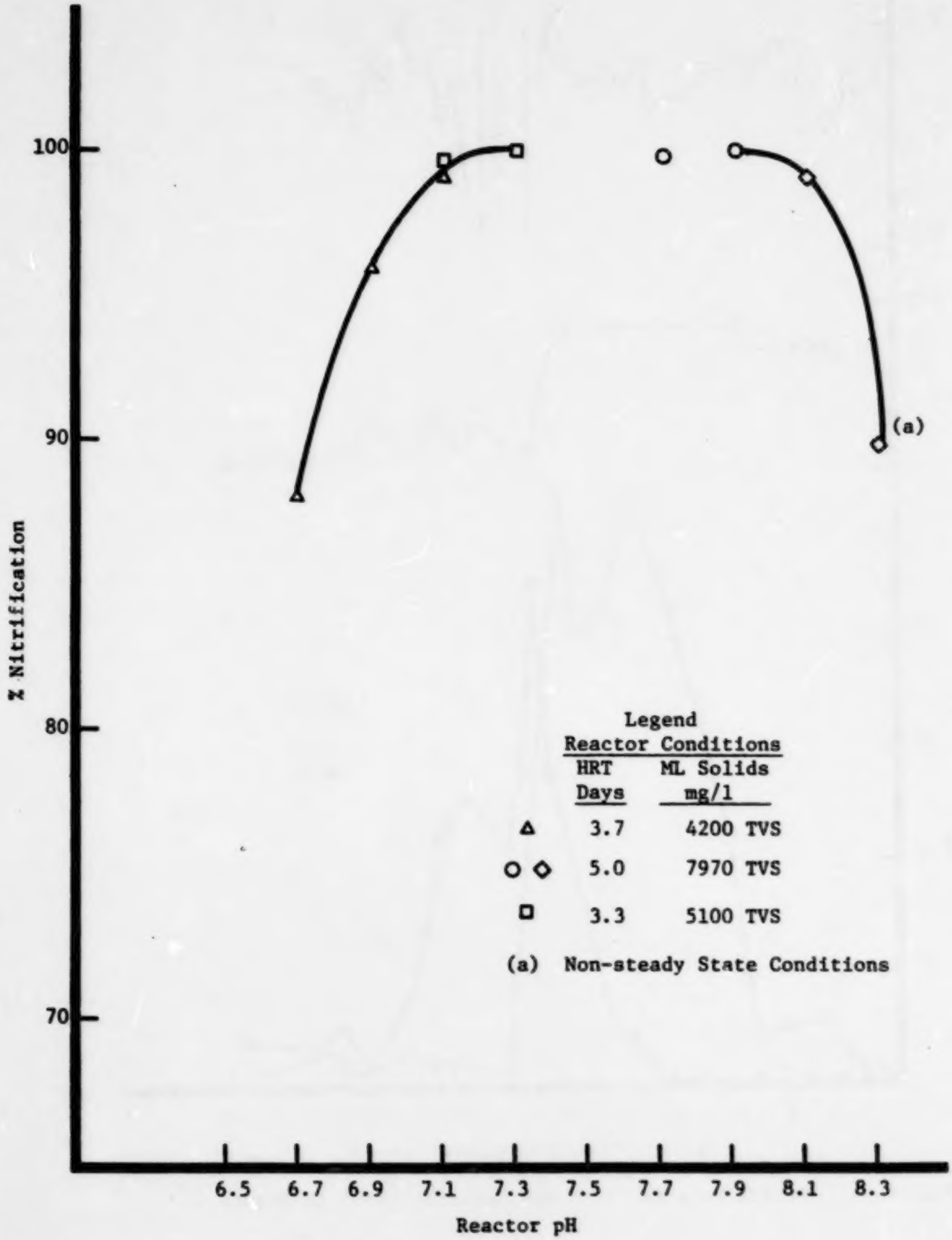
Thus, for a given wastewater stream and desired effluent quality, the size of the aeration basin can be related to the mixed liquor solids concentration using Equation 11. This equation indicates that the higher the mixed liquor sludge concentration the smaller the volume of the aeration basin.

pH and Alkalinity

Two of the experimental pilot reactors were operated over a range of pH conditions to determine the effect(s) of pH on nitrification, the results of which are summarized in Figure 8. It is noted that the range shown in Figure 8 is somewhat greater than the 7.0-7.5 range mentioned in the literature as being the optimum environmental condition for the maintenance of the nitrification reaction.(2) It is also noted that the sludge content of the two reactors was different and the reactor with the greater mixed liquor sludge concentration was used in examining the higher pH region. From Figure 5 it would be expected that the reactor with the higher sludge content would have a higher oxidation capacity. This greater oxidative capacity coupled with a long hydraulic residence time may have counteracted any negative effect at pH levels greater than 7.5. The result could be the higher efficiencies observed at pH 7.7 and 7.9 when compared to optimum efficiencies discussed in the available literature.

The data points at pH 8.1 and 8.3 on Figure 8 are also significant in that steady state conditions were not achieved during the experimental work suggesting that the real efficiency could have been lower than shown. The detailed data for these two data points are presented in Figure 9. From Figure 9, it can be seen that with a pH increase from 7.9 to 8.1, there was a slight increase in thiocyanate concentration. In addition, further

Figure 8. Effect of pH on Nitrification of Coke Plant Wastewaters.



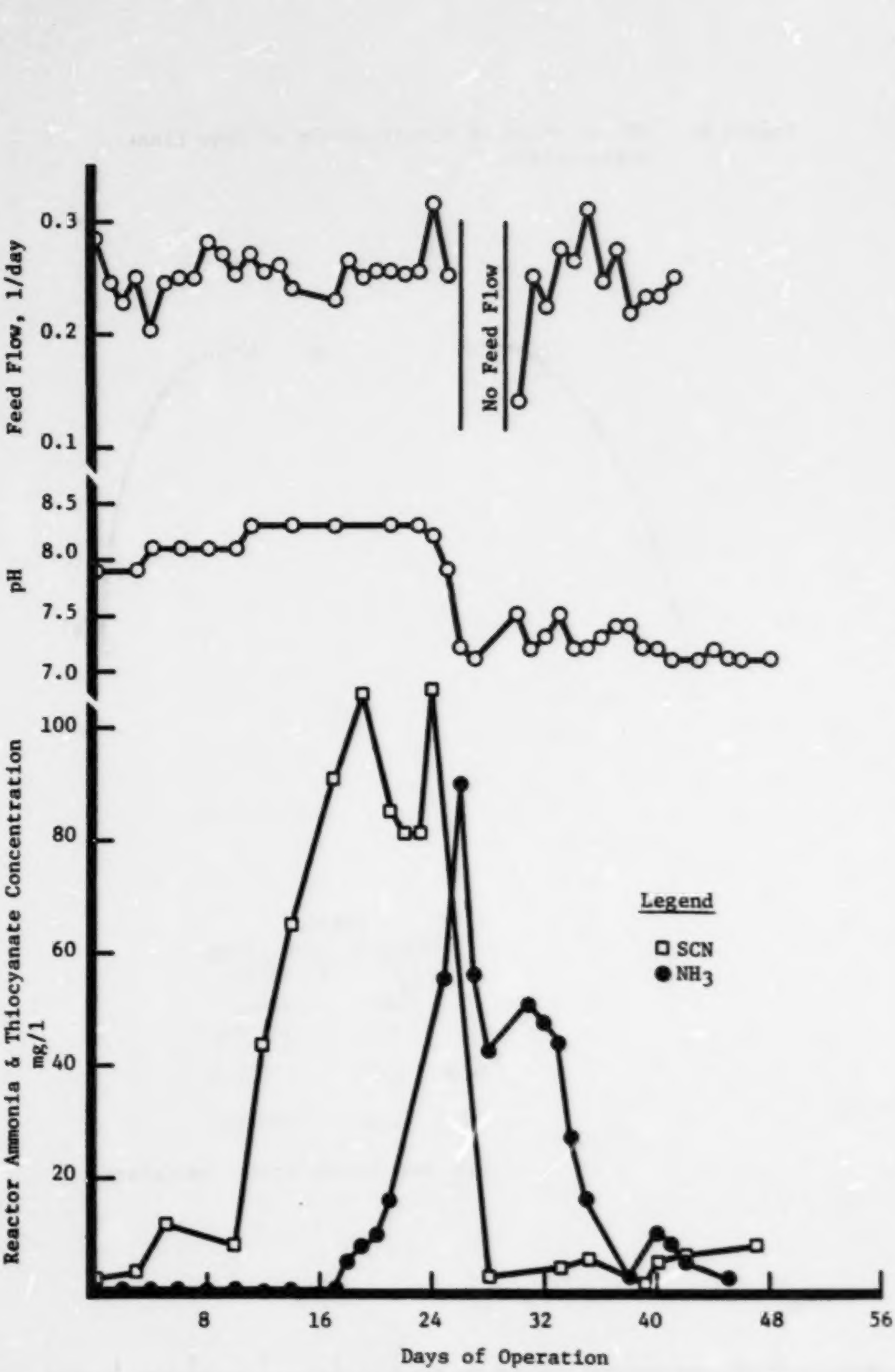


Figure 9. Detail Data for High pH Condition Shown in Figure 15.

increasing the pH to 8.3 resulted in a substantial increase in thiocyanate concentration. Decreasing the reactor pH from 8.3 to 7.2 resulted in an immediate reduction in the reactor thiocyanate concentration. In effect, high pH levels, >8.1, appear to adversely affect SCN degradation.

The mixed liquor thiocyanate concentration, possibly along with the synergistic effect of pH, appears to adversely affect the nitrification reaction. Deterioration of nitrification appeared at a thiocyanate concentration about 100 mg/l and pH of 8.3.

The effect of pH on the biological treatment process is further illustrated in Figure 10. Figure 10 represents the performance of a reactor receiving ammonia still waste as produced, i.e., the raw wastewater composition varies. Further, in this test sequence the feed flow rate also varied, as shown. The data in Figure 10 suggest the following: 1) both high and low pH conditions affect nitrification, 2) the adverse effect of low or high pH can be counteracted by decreasing the wastewater flow rate and 3) high pH conditions affect SCN degradation. In spite of the observed fluctuations, phenol treatment was 99.9% + effective, with effluent concentrations less than 200 μg/l.

The ammonia-nitrogen oxidation reaction produces acid according to the following equation:

$$NH_4 + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad (12)$$

The formed acid tends to decrease the pH of the reaction medium, and in order to maintain optimum reaction efficiency, alkalinity must be added to the system to neutralize the acid produced. Stoichiometrically, 7.14 units of $CaCO_3$ alkalinity are required to neutralize the acid generated from the oxidation of one unit weight of ammonia-nitrogen. A series of tests was conducted to determine the alkalinity requirements. Figure 11 presents the results of those tests and the alkalinity requirement A, can be estimated from

$$A = 4.46N - 517$$

where A = $CaCO_3$ alkalinity required, mg/l
N = nitrogen oxidized, mg/l

The correlation shows that 4.5 units of $CaCO_3$ alkalinity are required for every unit weight of nitrogen oxidized.

Dissolved Oxygen

In the course of the study, project efforts were taken to maintain all reactor dissolved oxygen levels greater than 1.0 mg/l. There was no deliberate effort to determine the effects of dissolved oxygen concentrations.

Temperature

The temperature studies covered the range from 60°F to 95°F. From the temperature evaluation it was determined that, 1) optimum reactor operating temperature is between 70°F and 80°F, 2) sludge oxidation occurs at 95°F, 3) normal

Figure 10. Performance of a Phenol-Nitrification Reactor Receiving As-Produced ASW.

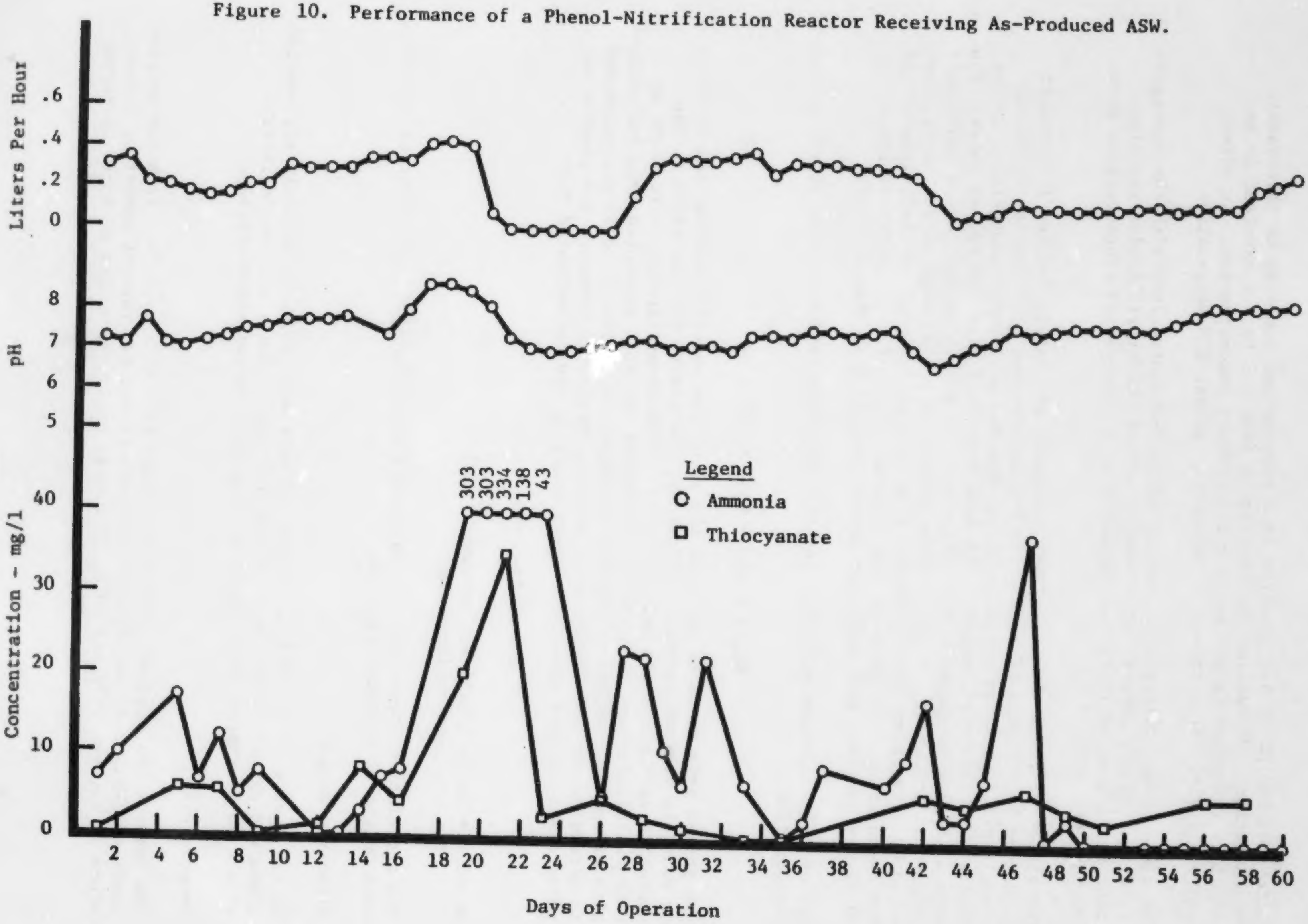


Figure 10. Performance of a Phenol-Nitrification Reactor Receiving As-Produced ASW. (continued)

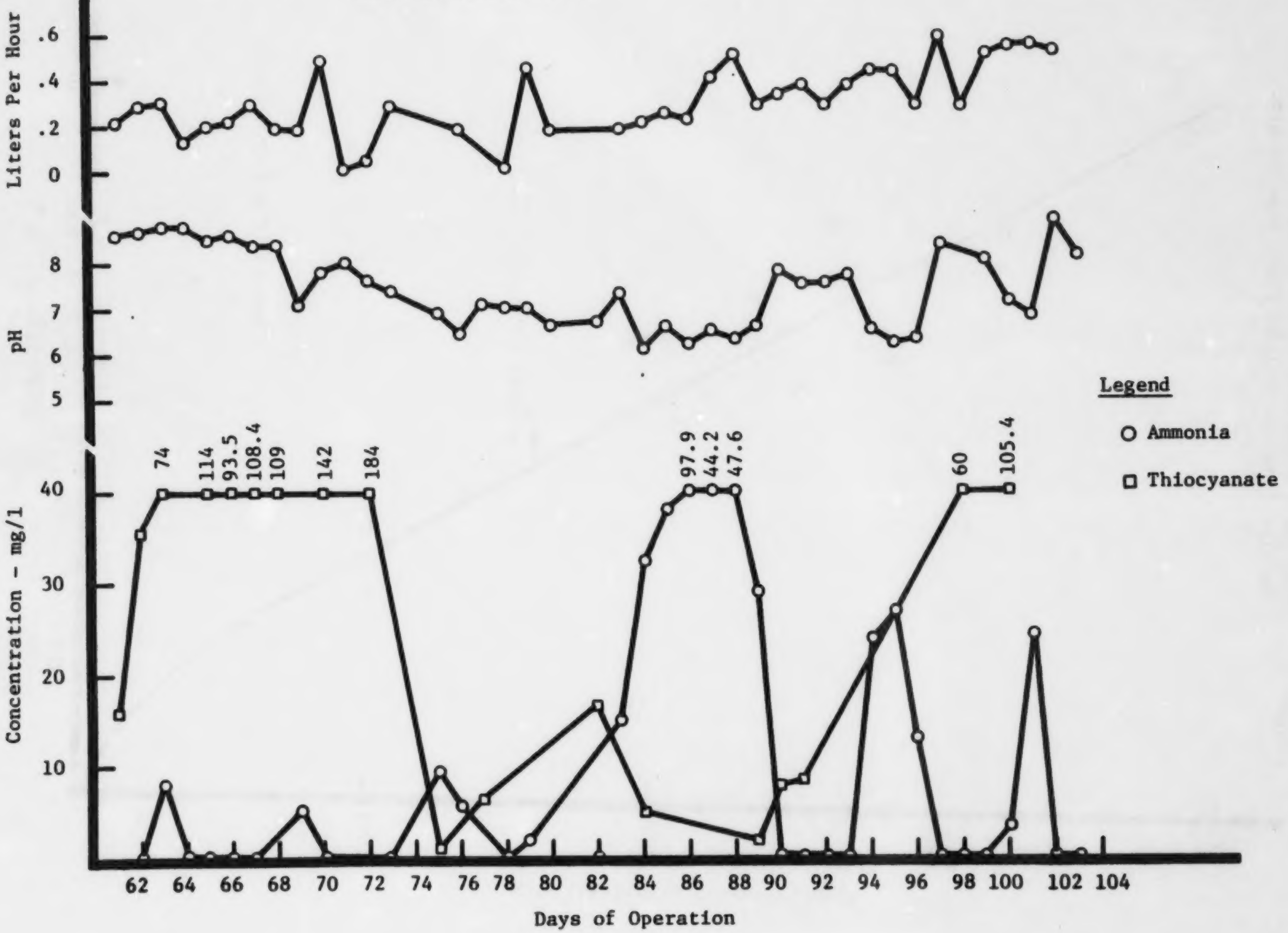
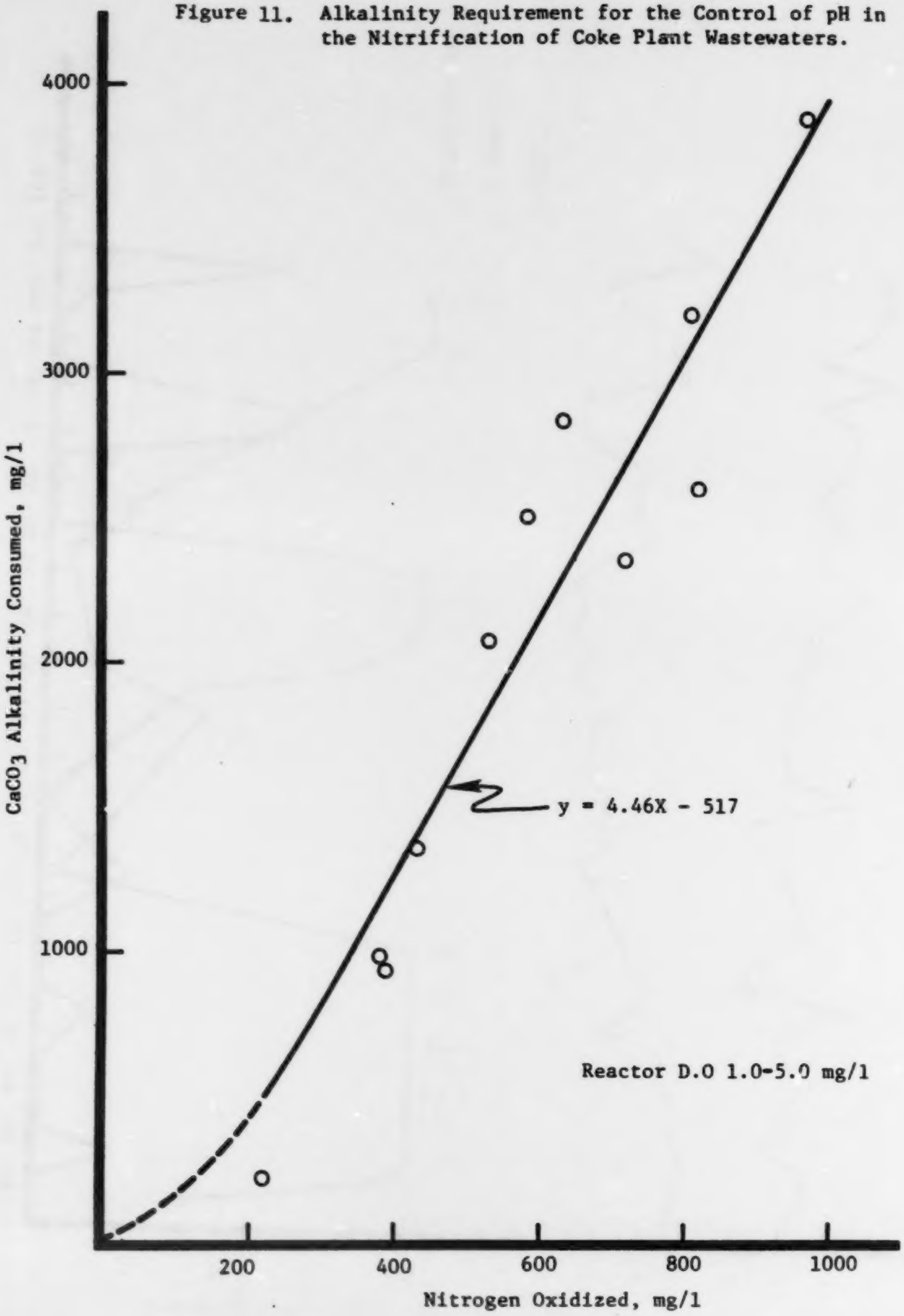


Figure 11. Alkalinity Requirement for the Control of pH in the Nitrification of Coke Plant Wastewaters.



operating residence times will have to be increased at reactor temperatures below 70°F to maintain nitrification and 4) phenol oxidizing bacteria may be adaptable to operating temperatures less than 70°F. Figure 12 shows the nitrogen oxidation rates for the temperatures of 95°F, 80°F, 70°F and 60°F. Optimum rate of nitrification was observed to be between 70°F and 80°F. Significant decreases in the oxidation rate occur outside this boundary. Extrapolation of the data line from the data point at 60°F into lower temperature ranges and observing all data points up to a temperature of 80°F indicates that the rate of nitrification increases with temperature throughout the range. However, when the reactor temperature was allowed to increase beyond the optimum range, the nitrification rate decreases possibly due to bacteria cellular destruction.

Figure 13 is a graphic presentation of the reactor concentrations of ammonia, phenol and thiocyanate at the evaluated temperatures. Although all data points are connected by straight lines, it is noted that system adjustments occurred between temperature changes. It was necessary to replenish the mixed liquor suspended solids in the reactor after the 95°F evaluation.

Only a short evaluation period for a temperature of 80°F was performed as prior experience during the initial phases of the project had shown that 80°F was near an optimum operating temperature. The intent of the temperature evaluation was to determine the stresses, if any, on the bio-process when the temperature was allowed to vary from the established optimum temperature.

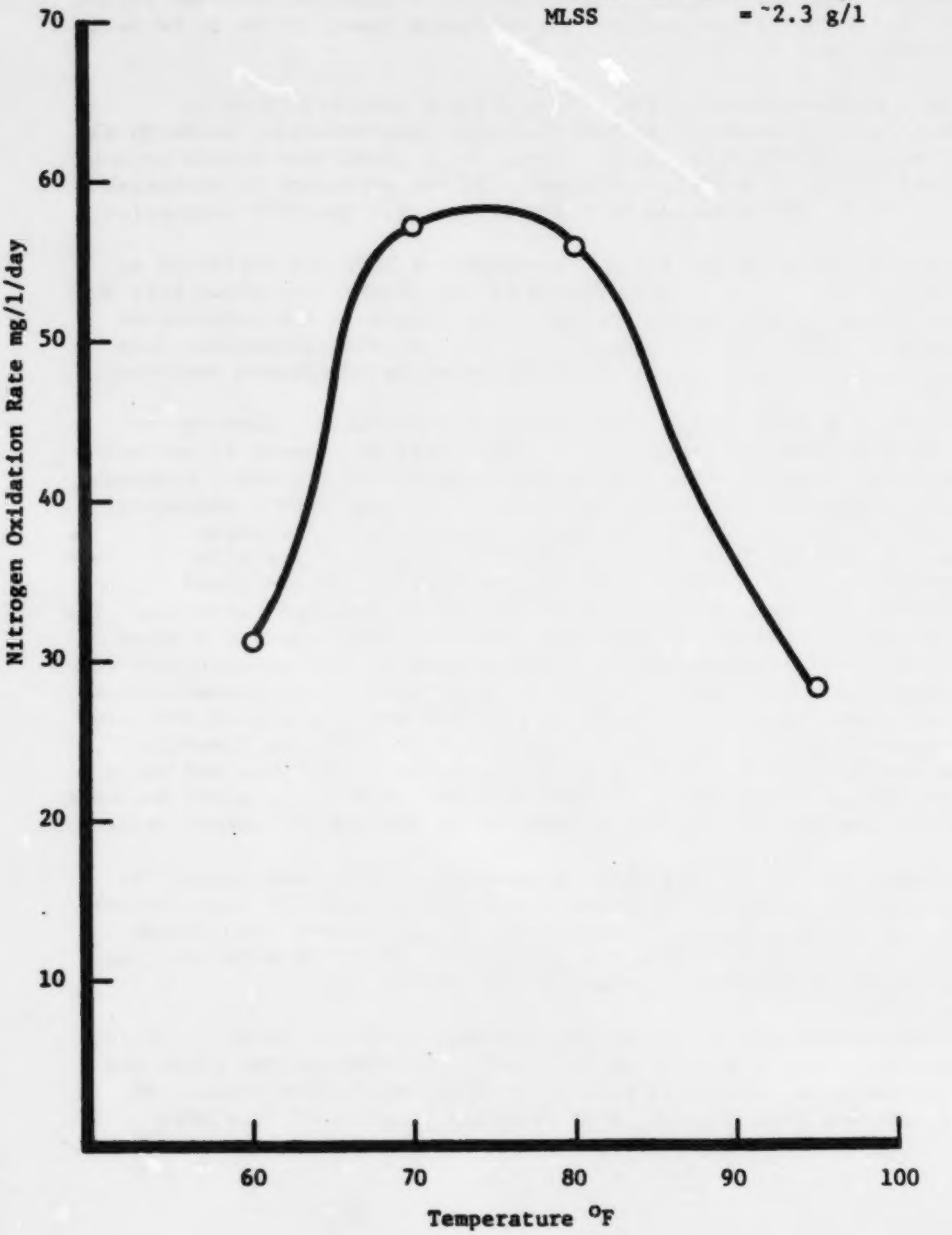
Two evaluations were made at the 95°F operating temperature, although only one set of data is shown in Figure 13. In the first experiment it was noted that a significant loss of mixed liquor suspended solids occurred, although no deliberate sludge wasting was being practiced. After twenty operating days, the reactor concentrations of ammonia, phenol and thiocyanate had increased significantly indicating that the biological functions had been severely inhibited. The obvious cause was the decrease in the mixed liquor suspended solids or a lack of micro-organisms for contaminant oxidation. The pilot reactor was replenished with sludge from the sludge bank to a mixed liquor suspended solids concentration corresponding to the concentration when the experiment originally began. Figure 14 shows volatile suspended solids concentration versus time and the reactor residual ammonia, phenol and thiocyanate concentration at an operating temperature of 95°F. An immediate decrease in the volatile suspended solids concentration was observed which continued for 20 operating days. Correspondingly, there was a sharp decrease in thiocyanate removal, followed by a decrease in ammonia and phenol oxidation.

It was concluded that at an operating temperature of 95°F (and above) the activated sludge experiences combustion (oxidation or cellular destruction) to a degree that renders the activated sludge system useless even though other parameters such as hydraulic residence time, pH and DO were held constant resulting in no external stresses to the bio-system.

In general, the mechanisms affecting the nitrogen oxidation rates below and above the optimum rates appear to be different. At temperatures below the optimum rate, bacterial action is reduced by lower metabolism rates. At temperatures greater than optimum, nitrification is affected by sludge

Figure 12. Nitrogen Oxidation Rate Versus Reactor Operating Temperature.

pH = 7.3
Retention Time = 5.3 Days
MLSS = ~2.3 g/l



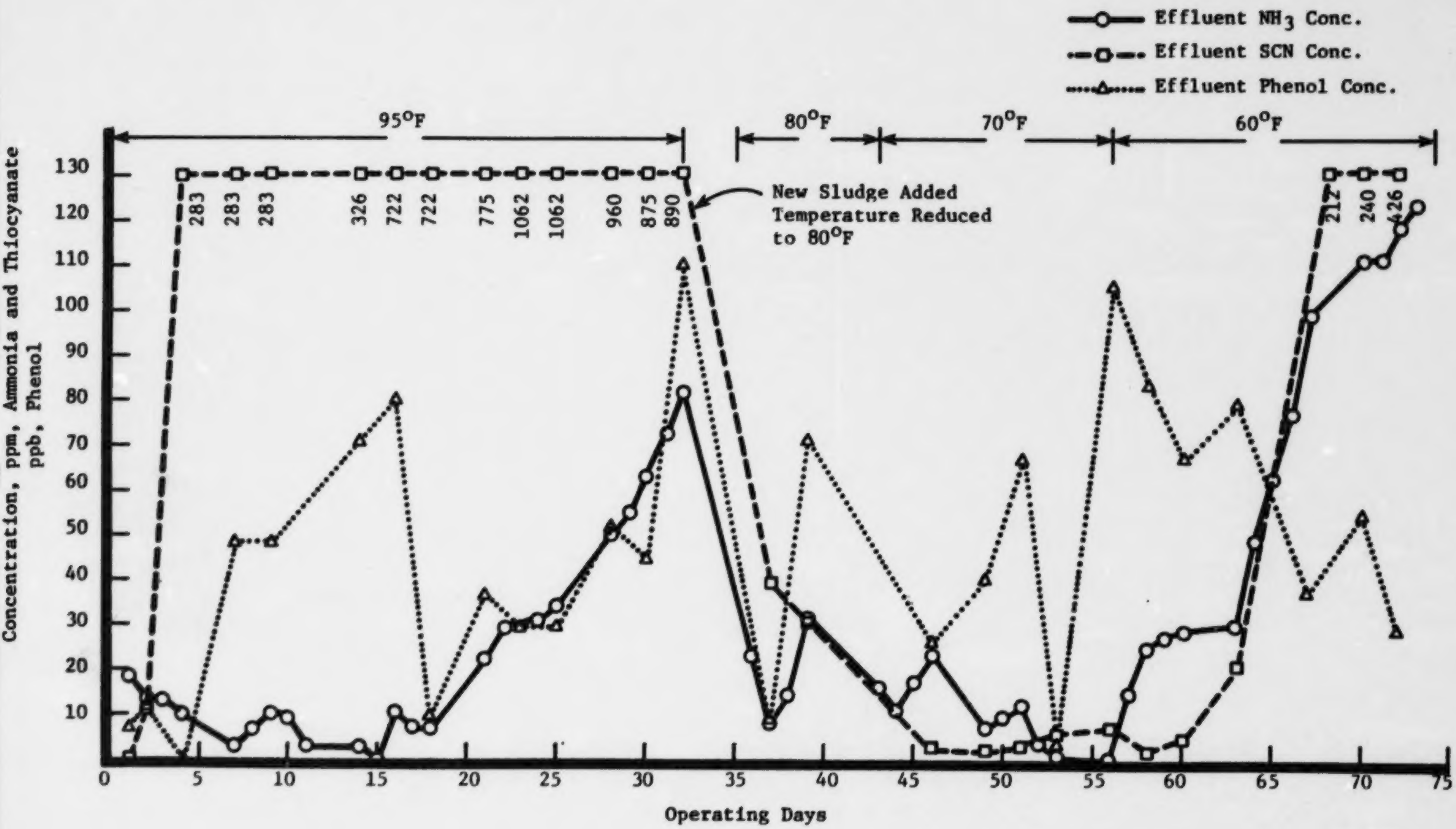
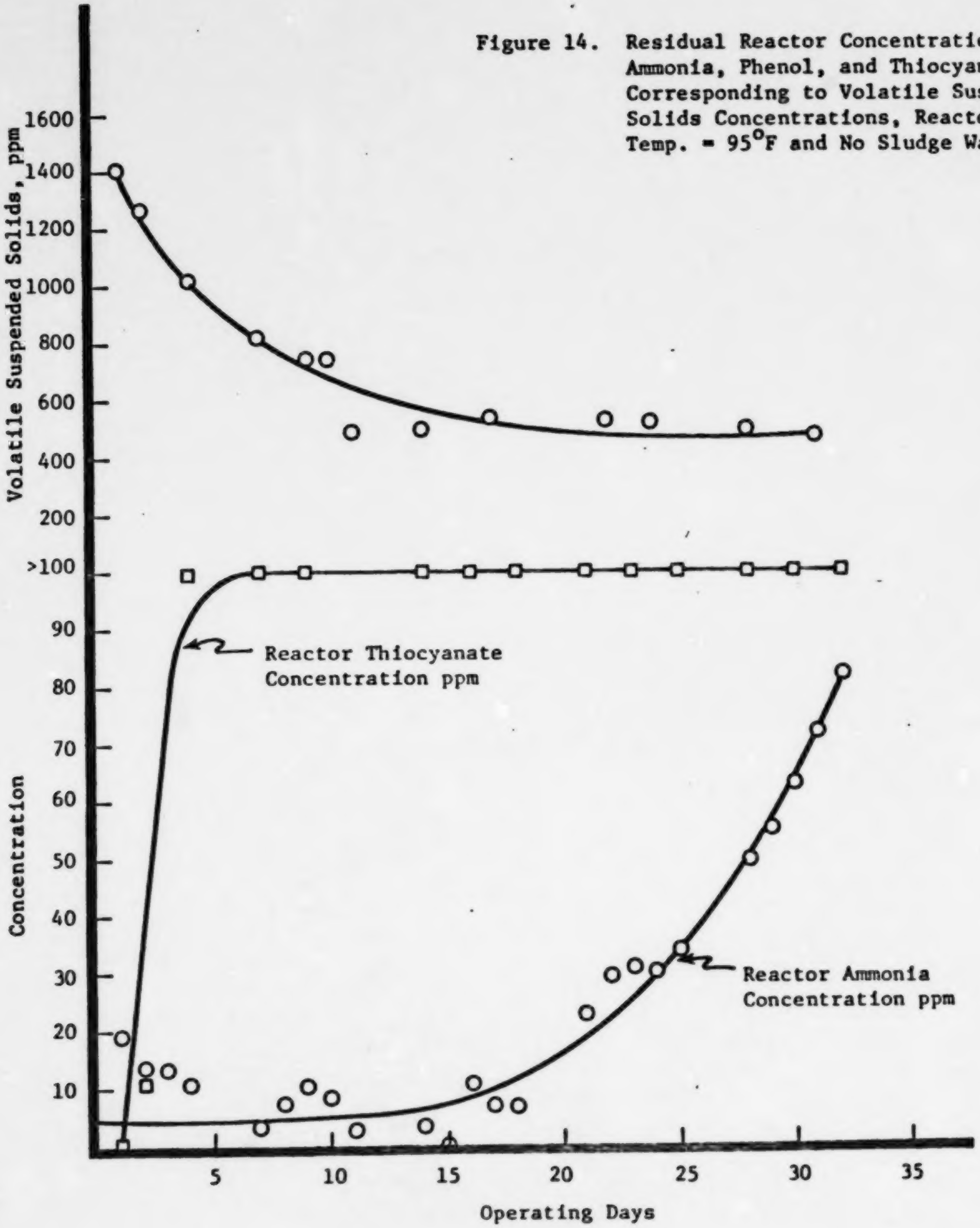


Figure 13. Residual Reactor Ammonia, Phenol, and Thiocyanate Concentrations at Various Temperatures.

Figure 14. Residual Reactor Concentrations of Ammonia, Phenol, and Thiocyanate Corresponding to Volatile Suspended Solids Concentrations, Reactor Temp. = 95°F and No Sludge Wasting.



oxidation reducing the quantity of bacteria available for contaminant removal.

To increase the oxidation rates at operating temperatures lower than optimum, the residence time could be increased. Increased residence times will simply allow for more contact time between the contaminants in the feed water and the bacteria operating at reduced metabolic rates.

One exception to the effect of temperature at lower temperatures (<70°F), is the apparent ability of the phenol oxidation organisms to adapt or acclimate to the lower temperatures as can be observed in Figure 13.

EFFECTS OF DIFFERENT COMPONENTS IN RAW WASTEWATER

Different components in coke plant wastewater were examined for their effects on the biological phenol-nitrification treatment process. The components examined were: 1) ammonia, 2) thiocyanate, 3) cyanide (free and complex), 4) light oil (by-product BTX), 5) sulfide and 6) phenol. The objective of examining the effects of these materials was to understand the biological process such that in the event of a shock loading upset condition, proper corrective measures could be implemented.

Ammonia

The effects of ammonia were examined by incrementally increasing the concentration of ammonia in the feed wastewater. Two pilot reactors, nos. 7 and 8, were used to (a) provide duplication of the observations and (b) to observe the influence of mixed liquor sludge on those effects.

Figures 15 and 16 present the chronological observations on ammonia and thiocyanate concentrations. Other pertinent data such as mixed liquor solids, hydraulic residence time, feed ammonia and ΣN_i, mean pH and N-oxidation rate, k, are presented. In Figure 15 it can be seen that with the reactor operating at a HRT ~5.2 days the feed ammonia concentration was increased from 210 mg/l to 510 mg/l in a 30 day period without any adverse effect on the effluent ammonia and thiocyanate concentration. It is also noted that k_A also increased from 56.0 mg/l/day to 104.5 mg/l/day. For the mixed liquor sludge concentration, the 56.0 mg/l/day oxidation rate was expected; however, the virtual doubling of the oxidation rate was not expected. Apparently, by increasing the ammonia content of the feed wastewater, a population shift in the sludge occurred, i.e., there was an increase in the number of nitrifying organisms.

Another interesting facet of the data shown in Figure 15, is the apparent failure. Up to the 35th day, the reactor functioned effectively, i.e., there were low concentrations of ammonia and thiocyanate in the treated wastewater. For the succeeding period, 36th to 50th day, the wastewater loading to the reactor was increased, hydraulic residence time of 4.15 days, resulting in a gradual increase in both ammonia and thiocyanate concentrations and the bioprocess appeared to be headed toward failure.

However, with a decrease in the reactor loading, hydraulic residence time of 5.5 days, for the final 10 days of the test, the ammonia concentration appears to be stabilized at 40 mg/l and tending toward even lower concentrations; the

Figure 15. Effect of Increasing the ΣN Load on Reactor No. 7.

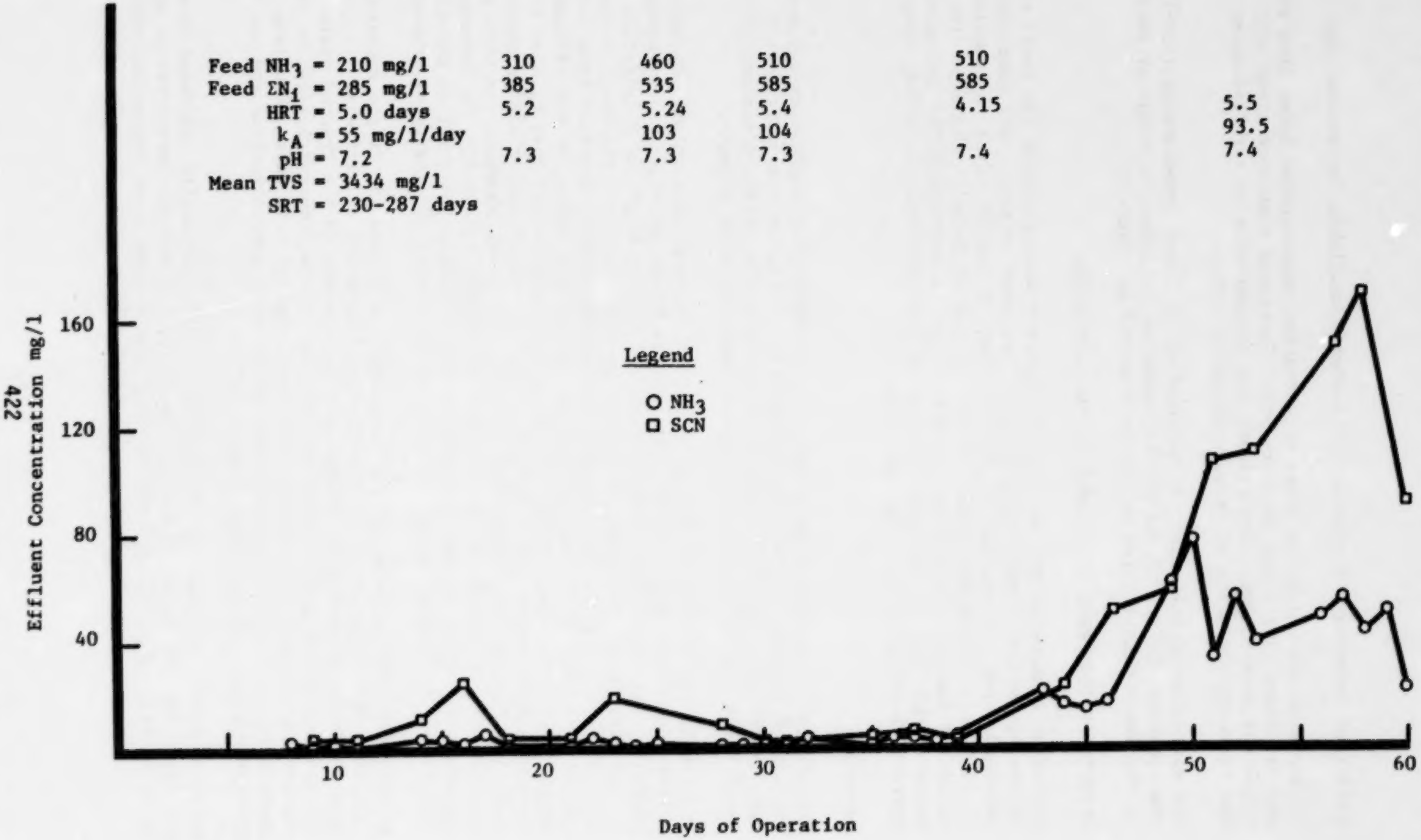


Figure 16. Effect of Increased ΣN Loading on Reactor No. 8.

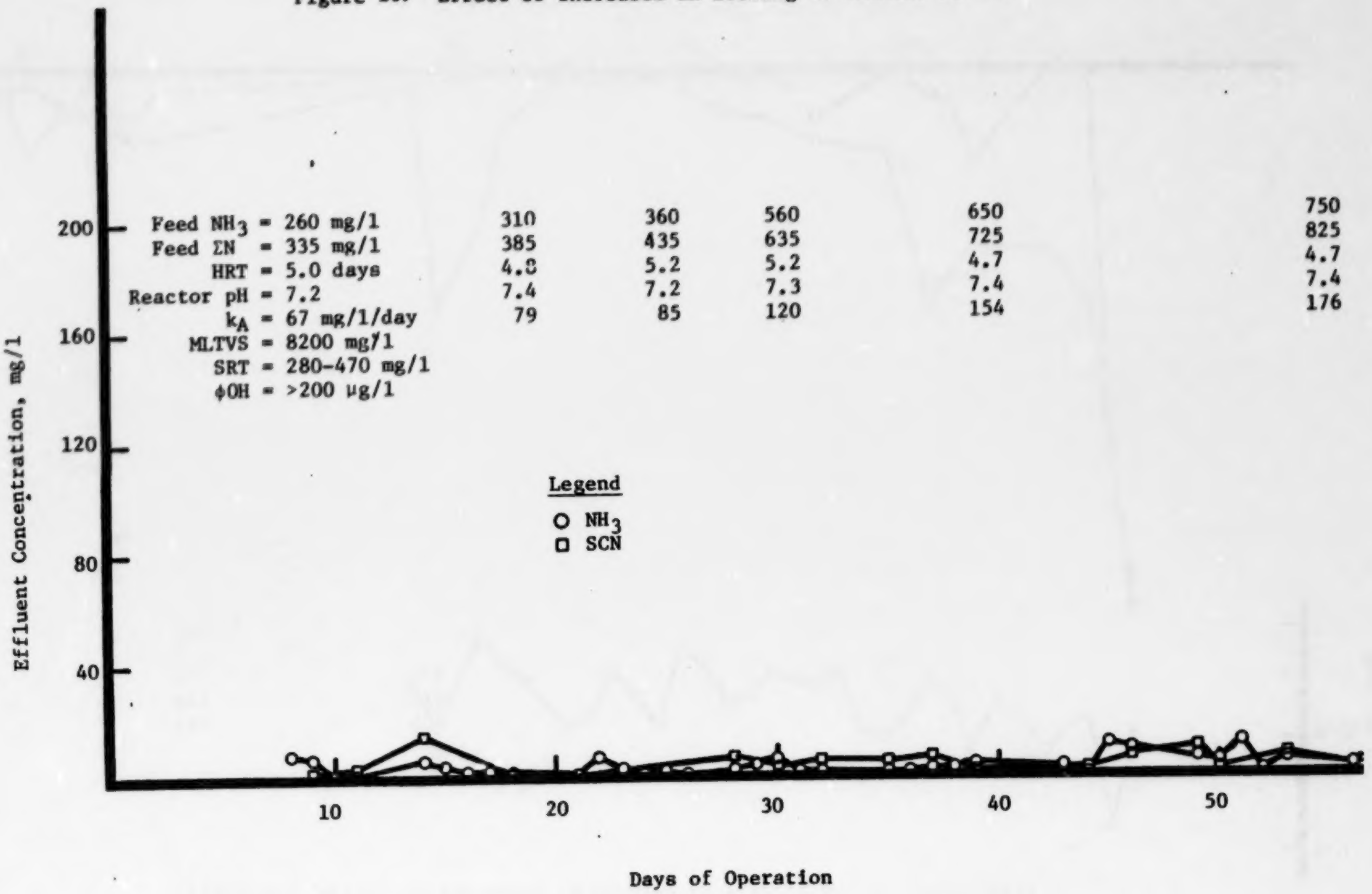
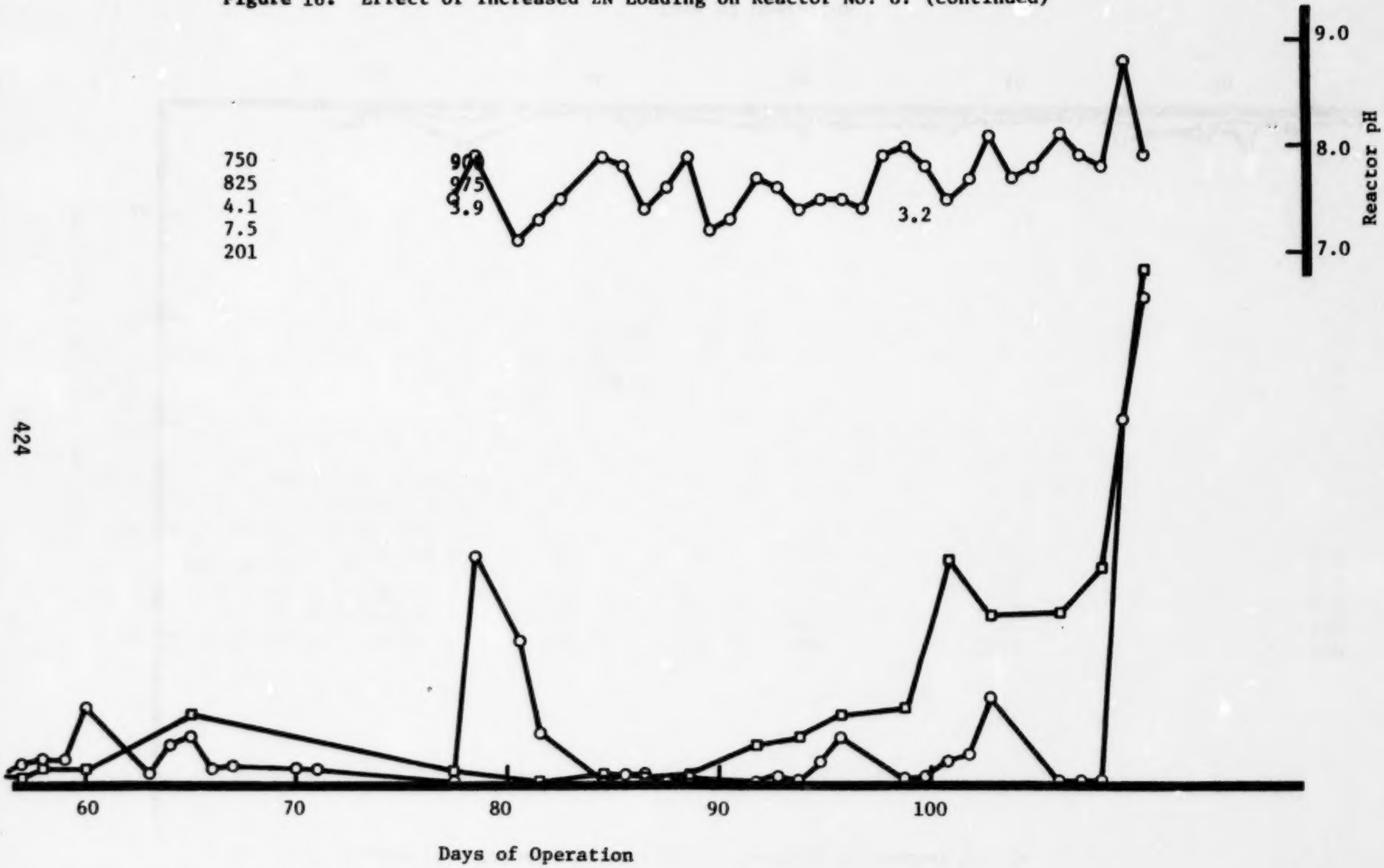


Figure 16. Effect of Increased ΣN Loading on Reactor No. 8. (continued)



thiocyanate concentration while high also, appeared to have peaked and began to decline. During the final 10 days, the average k was 93.5 mg/l/day which compares well with the 104 mg/l/day observed prior to the 35th day. In effect the micro-organisms were effectively removing the substrate material both in the feed and that which had accumulated in the reactor. The reactor operational adjustment of reducing the loading rate (increasing the hydraulic residence time) was an effective way of achieving recovery from the upset.

In the duplicate experiment, chronological data shown in Figure 16, the mixed liquor sludge was about 8200 mg/l TVS. With this reactor sludge concentration, an estimate of k_A is about 120 mg/l/day from Figure 5. Thus, the effective treatment during the initial 40 days of the experiment was not unexpected. However, with the gradual increase in nitrogen loading to the reactor, feed ammonia of 750 mg/l and ΣN of 825 mg/l, k_A increased to about 200 mg/l/day; again almost a two fold increase. On the 78th day, the reactor loading was again increased this time both in feed concentration, ΣN of 975 mg/l, and hydraulic residence time of 3.9 days. The reactor responded with an immediate increase in ammonia concentration which gradually decreased with time. At this point, the reactor appeared to be operating in a stabilized manner. On the 99th day, the reactor loading was again increased by decreasing the hydraulic residence time to 3.2 days. This increase in loading resulted in an increase in the reactor thiocyanate concentration and an eventual increase in ammonia concentration. The residual concentration of contaminants in the reactor increased to what appeared to be a failure of the system for nitrogen removal.

From the two series of experiments shown in Figures 15 and 16, it can be concluded that the wastewater feed ammonia concentration per se had little effect on the effectiveness of the treatment reactors. However, other factors such as loading rates, hydraulic residence time, reactor pH and sludge concentration greatly influence the treatability of feeds with high concentrations of ammonia.

Thiocyanate

The effects of thiocyanate were examined in two reactors, no. 3 and no. 4. In reactor no. 4, the feed thiocyanate concentration was incrementally increased from the normal 300 mg/l to 500 mg/l. This reactor was observed for a period of 55 days and there appeared to be no adverse effect on the performance of the reactor as a result of the increased concentration of thiocyanate in the feed wastewater. Table 3 presents the performance data for this test, and the average effluent quality for the test was as follows: 1) ammonia concentration = 5 ± 5 mg/l, 2) thiocyanate concentration = 9 ± 16 mg/l and 3) phenol concentration = 77 ± 219 μg/l. The reactor operating conditions were: 1) hydraulic residence time = 3.9 ± 1.0 days, 2) mixed liquor sludge = 3465 mg/l TVS, 3) k_A = 63 mg/l/day, 4) pH = 7.2 ± 0.2 and 5) temperature = 80-90°F.

Reactor no. 3 was used to examine the effect of direct spiked addition of thiocyanate on the performance of the bio-process. Table 4 presents the performance data for this series of tests and the indications are that spiked concentrations of thiocyanate up to 40 mg/l did not have any adverse effect on the reactor operating at the conditions shown.

Table 3. EFFECT OF FEED SCN CONCENTRATION ON PERFORMANCE OF A REACTOR WITH 3465 mg/l TVS

			Reactor Concentration[b]			Feed[a]
Day of Operation	Reactor pH	HRT, Days	NH_3 mg/l	SCN mg/l	ϕOH µg/l	SCN mg/l
1	7.2	6.2	6			300
2	7.0	5.3	8			300
3	7.1	4.7	5	8	62	300
4	7.0	4.3	3			300
5	7.2	4.2	9		20	300
6	7.0	4.0				300
7	7.1	4.5				300
8	7.1	4.8	6	12	30	350
9	7.1	4.5	6			350
10			7	3	0	350
11			5			350
12			3	5	0	350
13						350
14						350
15	7.0	6.7	4	4	16	400
16	7.3	4.2	4			400
17	7.1	3.6	6			400
18	7.2	3.7	9	0	7	400
19	6.9	3.6				400
20	7.1	3.7	2	3	3	400
21	7.3	4.0	4			400
22	7.2	3.6	0	2	148	400
23	7.2	3.8	0			400
24	7.3	3.9	0	2	10	500
25	7.0	4.9				500
26	7.3	5.6				500
27	7.6	5.9	0	8	16	500
28	7.3	3.4	2			500
29	7.6	3.3	0	12	10	500
30	7.5	3.2	0			500
41	7.4	3.4	2	73	966	500
42	7.2	3.4				500
43	7.2	2.7				500
44	7.0	2.8	16	6	16	500
45	7.1	3.0	4			500
46	7.0	3.4	15	7	3	500
47	7.0	3.2	10			500
48	7.4	3.4	0	7	2	300
49	7.2	4.6				300
50	7.3	3.5				300
51	7.4	2.8	1	4	16	300
52	7.3	2.7	1			300
53	7.0	3.3	25	5	2	300
54	7.3	2.4	2			300
55	7.5	2.7	2	6	143	300
	7.2 ± 0.2	3.9 ± 1.0	5 ± 5	9 ± 16	77 ± 219	

(a) Other feed components NH_3 = 150 mg/l; ϕOH = 500 mg/l, Alkalinity = 60 mg/l
(b) Negative numbers observed due to variability in actual numbers.

Table 4. EFFECT OF SPIKE ADDITIONS OF SCN ON REACTOR PERFORMANCE(a)

			Reactor Concentration			Feed(b)
Day of Operation	Reactor pH	HRT, Days	NH_3 mg/l	SCN mg/l	ϕOH μg/l	SCN mg/l
0	7.2	4.8	3			
1	7.2	4.6	6	7	45	
2	7.2	4.1	4			
3	7.4	4.0	9		34	
4	7.1	4.4				
5	7.2	4.5				
6	7.2	4.0	16	1	16	10
7	7.2	4.3	9			10
8			13	8	11	10
9			6			20
10			8	6	10	20
11						-
12						-
13	7.0	3.7	8	3	0	20
14	7.3	3.9	7			30
15	7.2	3.3	7			-
16	7.2	3.8	9			-
17	7.0	4.1				40
18	7.1		0	2		-
19	7.6	4.0	5			-

(a) Reactor operated with 3790 mg/l TVS mixed liquor solids; temperature 74-86°F.

(b) SCN added to reactor to give concentrations shown.

In the test series shown in Figure 15 (ammonia concentration evaluation), where the reactor was operated at a pH ~7.4, the thiocyanate accumulated up to about 160 mg/l without any apparent adverse effects on the nitrification reaction. On the other hand, the data in Figure 9 (pH evaluation) show nitrification was adversely affected at a thiocyanate concentration about 90 mg/l at a pH of 8.3, indicating a possible synergism between thiocyanate concentration and pH. This possibility was further reinforced by the observations shown in Figure 16 (ammonia concentration evaluation) where the eventual reactor failure could be attributed to the combined effect of high pH and high thiocyanate concentration.

Free Cyanide

The coke plant wastewater used in this study program contained less than 0.1 mg/l of free cyanide, CN_f, and to determine the effect of this material, the feed water was spiked to 40 mg/l CN_f. The response of the biological treatment system to the free cyanide spiked feed is shown in Figure 17. Because of the generally low level of free cyanide in the wastewater, the microorganisms were not fully prepared to respond to the new feed. The result was an accumulation of free cyanide in the reactor. The presence of free cyanide adversely affected the nitrification reaction resulting in the ammonia concentration increasing to about 120 mg/l. The most surprising feature of this experiment was the ability of the nitrifying organisms to acclimate or tolerate the high free cyanide concentration, 12 mg/l. This acclimation or tolerance resulted in the rapid reduction of the reactor ammonia concentration. Throughout this test, the reactor thiocyanate concentration was about 2 mg/l and the phenol concentration was less than 0.2 mg/l. This observation was surprising because it was previously reported(1) that 0.5 mg/l free cyanide completely inhibited the nitrification reaction and 3.0 mg/l inhibited the thiocyanate reaction. However, it does demonstrate that the nitrifying organisms can tolerate and adapt to high concentrations of free cyanide.

Complex Cyanide

The complex cyanide content of the wastewater used varied from 6 to 108 mg/l. Furthermore, it was noticed that these compounds tended to pass through the biological reactor unaltered and without exerting any adverse effect on the reactor performance. In spite of these observations, a test reactor was assembled to monitor the effect of complex cyanide. The raw wastewater was spiked with potassium ferri-cyanide, $K_3Fe(CN)_6$, to produce a complex cyanide concentration of 84 mg/l. Figure 18 shows the complex cyanide concentrations observed during the operation of the test reactor and compares these observations with a predicted profile. The basis for the prediction profile are: 1) no alteration of complex cyanide, 2) operating conditions of the reactor, i.e., hydraulic residence time of 3.9 days and 3) an initial complex cyanide concentration of 25 mg/l in the reactor. This prediction profile is mathematically described as:

$$C = C_i - 59e^{-0.256T} \qquad (13)$$

There is no real reason for the difference between the prediction and observed values, and the magnitude of these differences does raise some questions regarding the ineffectiveness of biologically degrading the complex ferrocyanides. In the course of this test, the following are the reactor conditions: 1) ammonia concentration - 3.7 ± 2.6 mg/l, 2) thiocyanate concentration =

Figure 17. Effect of Free Cyanide on Nitrification.

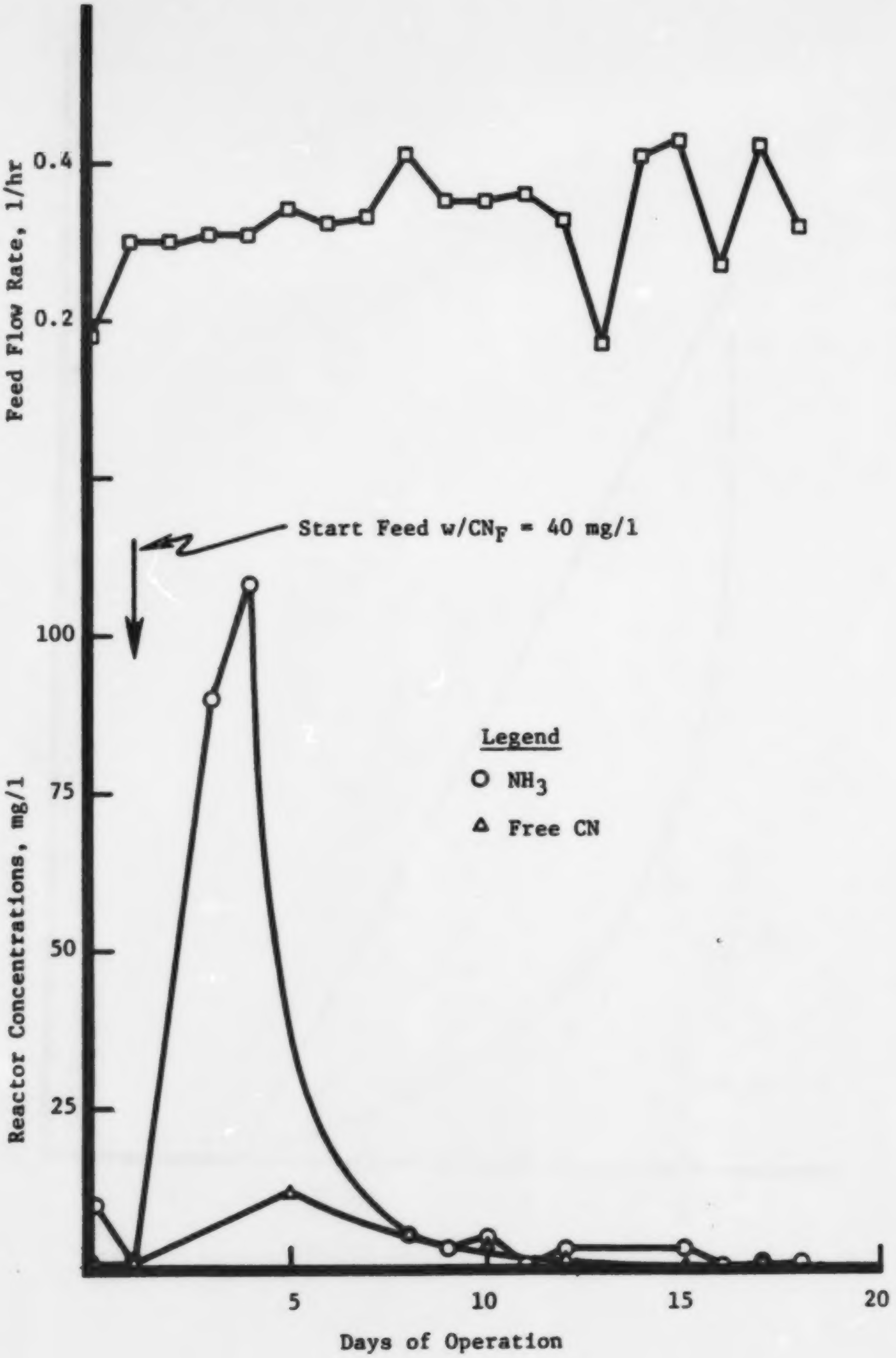
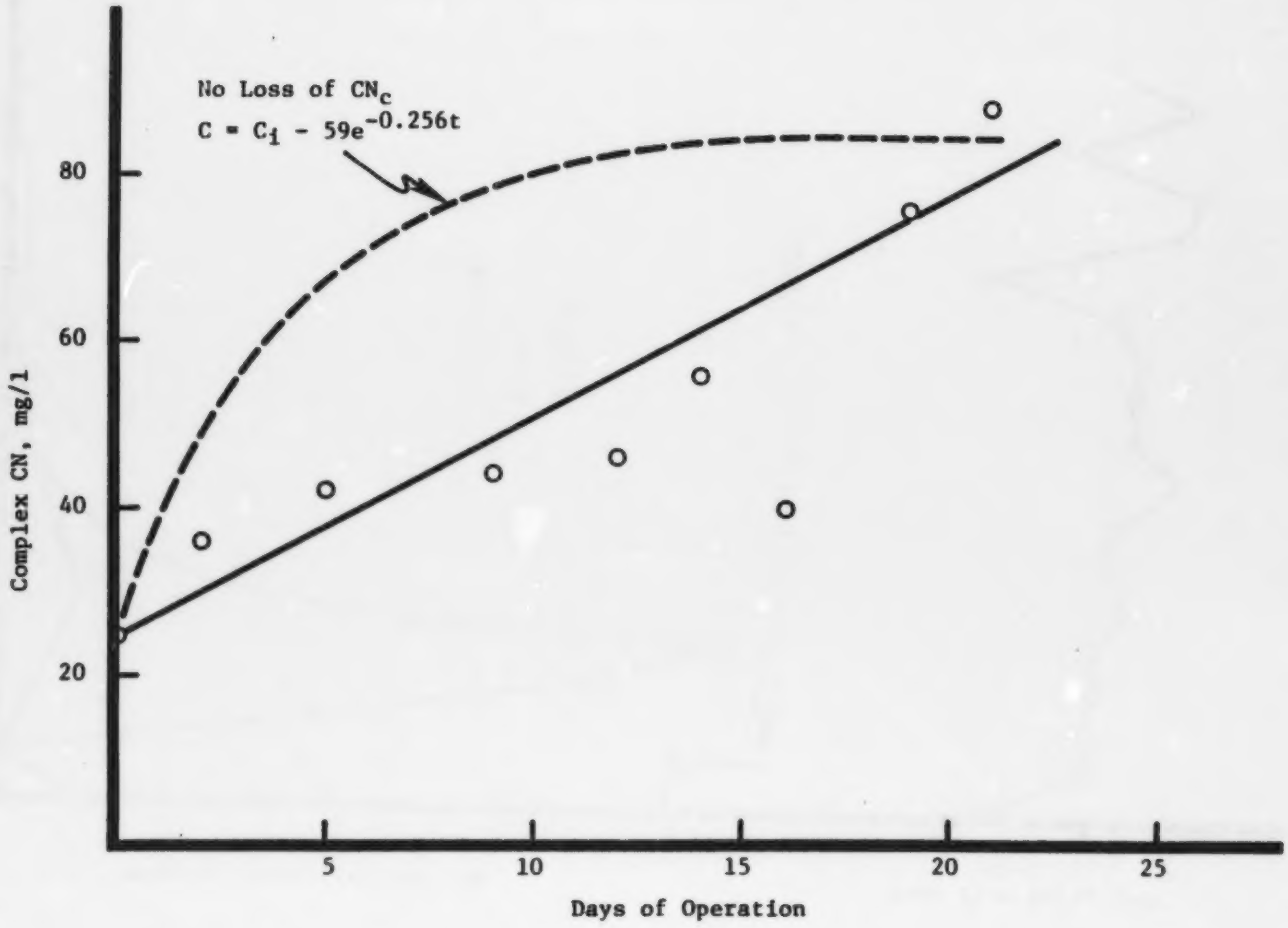


Figure 18. Complex Cyanide Profile Through Reactor No. 7.



3.6 ± 2.6 mg/1, 3) phenol concentration = 32 ± 26 μg/1, 4) hydraulic residence time - 3.9 days, 5) pH = 7.3 ± 0.2, 6) temperature = 80-90°F and 7) reactor dissolved oxygen concentration = >1.0 mg/1.

Light Oil

In the by-product operation of coke plants, light oils are produced. These oils are mixtures of benzene, toluene and xylene (BTX). In the course of these product operations, there is always the possibility that some of these light oils could reach the wastewater treatment system. With this possibility in mind, the effects of these light oils on the performance of the biological treatment process were examined. Because these light oils are nearly immiscible in the wastewater, it was believed that they would enter the biological treatment system as a "slug." Thus the procedure for this evaluation was to add certain quantities of the light oil directly to the reactor.

The performance data for the test reactor are presented in Table 5. Despite the two ammonia peaks at days 2 and 25, the overall performance data appear to be very similar to data obtained from control reactors maintained during the study. In effect the light oil does not appear to have any direct adverse effect on the nitrification reaction.

There is a potential for an indirect adverse effect, i.e., reduction of the oxygen transfer and mixing capabilities of the aeration equipment. Light oils entering the aeration basin could change the surface chemistry characteristics of the mixed liquor; the most likely characteristic which could be altered is the surface tension of the liquor. A severely decreased surface tension could adversely affect both mixing and oxygen transfer.

Sulfide

In most coke plants where vacuum-carbonate desulfurization is practiced, the blowdown from this unit is processed through the ammonia still with the waste ammonia liquor. In the free leg still, almost all of the acid gases including H_2S are removed. The ammonia still waste used in the course of this study contained relatively low concentrations of sulfide, about 25 mg/1. However, there is always the potential of high sulfide containing wastewaters being inadvertently routed directly to the wastewater treatment system.

The effects of a wastewater containing high concentrations of sulfide were examined by progressively increasing the sulfide content of the feed wastewater from the normal 25 mg/1 to 500 mg/1. Figure 19 summarizes the results of this evaluation showing the feed wastewater sulfide concentration had virtually no effect on the reactor ammonia, thiocyanate and phenol concentrations. It was, however, observed that the wastewater sulfide tended to suppress the pH of the reactor requiring more frequent measurement and control.

Direct addition of sulfide to concentrations up to 40 mg/1 to another test reactor also had no effect on the treatment process.

Throughout the course of this study program the reactor effluent sulfide concentrations were generally less than 0.5 mg/1.

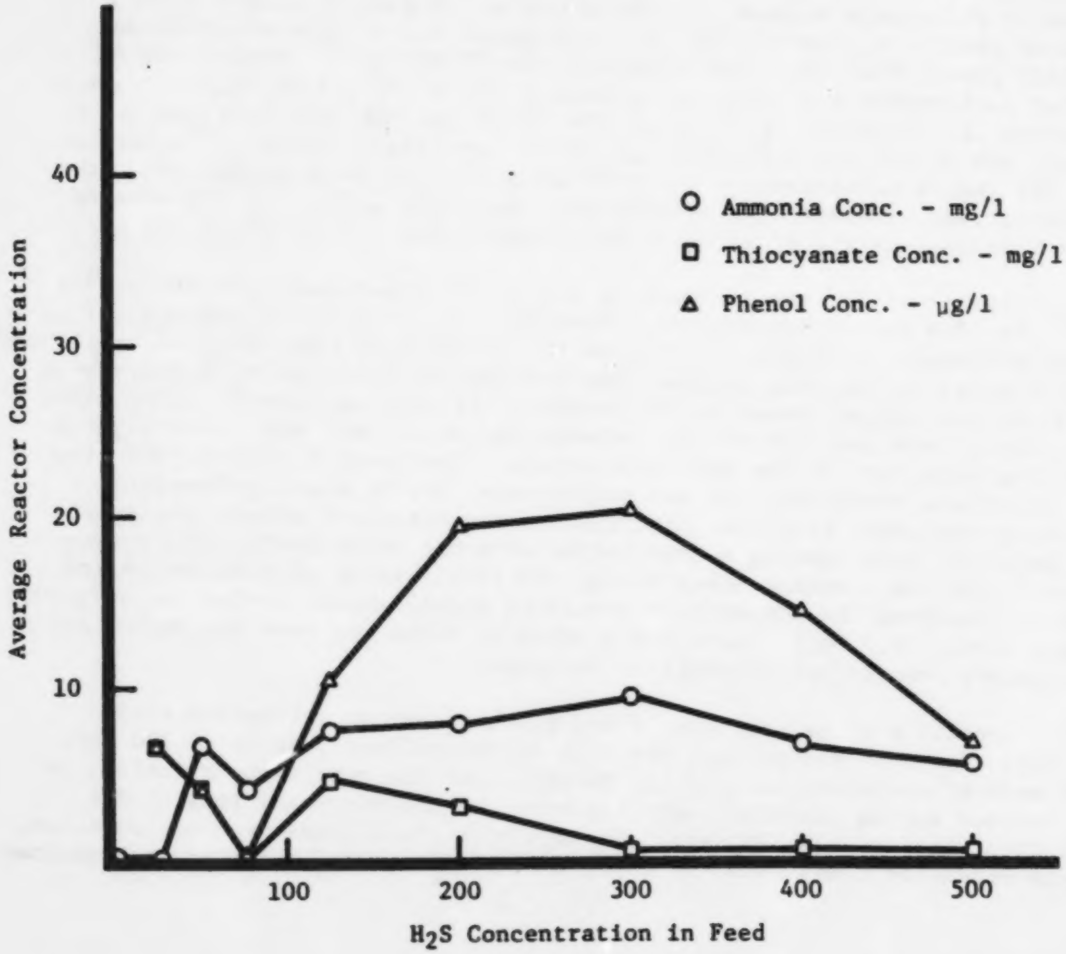
Table 5. EFFECT OF LIGHT OILS ON THE PERFORMANCE OF A SINGLE-STAGE PHENOL-NITRIFICATION REACTOR[(a)]

			Reactor Concentration			
Day of Operation	Reactor pH	HRT, Days	NH_3 mg/l	SCN	ϕOH μg/l	Oil Addition[(b)] mg/l
1	7.1	4.3	6	2	0	10
2	7.1	4.0	21	4	0	
3	7.2	4.3	5	1	0	
4	7.2	4.2	2	0	0	10
5	7.2	4.7	4			
6	7.2	4.3	-			
7	7.2	4.2	-			20
8	7.2	4.2	10	0	41	20
9	7.2	3.9	5			50
10	7.2	3.9	6	5	20	
11	7.2	4.1	7			
12	7.2	4.0	6	0	34	100
13	7.2	3.8	-			
14	7.1	4.7	-			
15	7.0	4.3	2	0	10	200
16	7.3	4.1	8			
17		4.2	6	4	20	
18	7.2	4.0	10			
19	7.2	3.6	7	0	3	500
20	7.2	4.1	-			
21	7.3	3.9	-			
22	7.3	3.7	3	3	92	
23	7.2	3.9	3			
24	7.3	4.2	6	0	20	1000
25	7.5	4.0	22			
26	7.6	3.8	8	5	30	
27			-			
28			-			
29			6	5	45	1500
30			5			
31			6	9	45	
32			10			
33			4	2	13	
34			8			
35			4			
36	7.2	2.9	10	4	0	
37	7.1	4.0				2000
38	7.2	3.5	6	0	13	
39	7.1	3.5	8			
40	7.0	3.2				
41	7.4	3.1				
42	7.6	3.7				
			7 ± 5	3 ± 3	23 ± 24	

(a) Standard Feed: NH_3 = 150 mg/l; SCN = 300 mg/l; ϕOH = 500 mg/l; Reactor Mixed Liquor Solids = 4330 mg/l VSS; Temp. ~74-84°F; Reactor DO >1.0 mg/l

(b) By-product Light Oil added directly to reactor in amounts to yield concentration shown.

Figure 19. Effect of Sulfide on Nitrification of Coke Plant Wastewaters.



Phenol

Phenol is a major constituent of coke plant wastewaters. The concentration of phenol in the wastewater depends on the type of coal being processed, the coking operation and the by-product recovery practice. The phenol concentration of coke plant wastewaters could be as high as 2000 mg/l. The ammonia still waste used in this program contained an average of about 120 mg/l. This concentration was adjusted to 500 mg/l for the standard feed. The effect of phenol on the performance of a phenol-nitrification reactor was examined from two directions; 1) spike additions to the reactor and 2) progressive increases in the feed phenol content.

Spike Additions. Phenol was added directly to the reactor in amounts which would produce a predetermined instantaneous reactor concentration. The additions were made in progressive increments starting from 0.5 mg/l up to 20 mg/l. Table 6 presents the data for this series of tests and the indications are that the nitrifying organisms were capable of acquiring tolerances up to about 30.0 mg/l without adversely affecting nitrification.

Increases in Feed Phenol. The effect of increased feed wastewater phenol content was examined in reactor nos. 5 and 6. The mixed liquor solids were the major difference between the two reactors. Figure 20 presents the performance profile for reactor no. 5. Throughout the 40 days of operation with the high phenol feed there was effective nitrification and phenol removal. Similar performance was observed in reactor no. 6, data from which are shown in Figure 21. However, it is noted that after the 30th day both the thiocyanate and phenol concentrations gradually increased. While it is evident that the phenol concentration was increasing it must be recognized that the concentrations were still relatively low, about 200 μg/l. The thiocyanate concentrations, on the other hand, were significantly high, about 150 mg/l.

The precise cause for the increase in phenol and thiocyanate concentrations after the 30th day is not evident. However, the inability to account for 81% of the wastewater nitrogen, alludes to the possibility that denitrification might have occurred during this period. Denitrification would occur if there were low dissolved oxygen levels in the reactor. If this was the situation, then there could have been competition between the nitrifiers and the thiocyanate oxidizing organism for the available oxygen. The results tend to show that the nitrifiers prevailed. It was unfortunate, due to dissolved oxygen measuring equipment problems, that the reactor dissolved oxygen levels which are generally taken during a test series were not taken during this evaluation. However, the few readings taken during the final stages of this evaluation somewhat confirms the supposition presented above, where, at the low dissolved oxygen level, ~0.5 mg/l, there was a definite trend for both the phenol and thiocyanate concentration levels to increase.

In the operation of reactor nos. 5 and 6, there was no deliberate sludge wasting. The only sludge lost was that in the effluent, about 80-100 mg/l. This mode of operation insured the retention of the nitrifying organisms in the reactor and is quantitatively expressed by the extremely long sludge retention times of 179-325 days. Under a more traditional mode of operation, sludge retention times of 30-50 days, the nitrifiers and thiocyanate organisms

Table 6. EFFECT OF SPIKE ADDITIONS OF PHENOL ON THE PERFORMANCE OF A PHENOL-NITRIFICATION REACTOR(a)

Day of Operation	Reactor pH	HRT, Days	Reactor Concentration (mg/l) NH3	SCN	ϕOH	ϕOH Addition(b) (mg/l)
0	7.4	4.0	0	2	0.05	
1	7.5	3.9	0			
2	7.6	4.3	0	2	0.12	
3	7.4	4.0				
4	7.4	4.3				
5	7.4	4.4	0	47	0.05	0.5
6	7.4	3.1	0			0.5
7			0	38	0.02	0.5
8			5			1.0
9			0	*(c)	14.75	1.0
10						
11						
12	7.3	3.6	0	*	2.32	10
13	7.5	4.3	0			10
14	7.6	4.3	0	*	20.60	
15	7.6	4.3	0			
16	7.5	4.3				20
17	7.2	4.3	24(d)	*	17.00	
18	7.6	4.1	25(d)			
19	7.4	4.2	26(d)	*	29.50	
21	7.3	3.2	0	*	*	
22	7.6	4.1				
23	7.4	4.6	0	*	0	
24	7.5	4.8				
25	7.8	4.9	0	*	21.21	

(a) Reactor operation conditions:

- Average mixed liquor solids = 3620 mg/l TVS
- Temperature
- All sludge produce was retained in the reactor, except for that lost in effluent ~100 mg/l SS. Approximate SRT ~134 days.

(b) Phenol added directly to reactor in quantities which would produce concentrations shown. Additions were made on days shown only.

(c) Analytical result was unrealistic and questionable.

(d) Reactor DO was ~0.2 mg/l. Generally the DO was >1.0 mg/l.

Figure 20. Effect of High Feed Phenol Concentration on Nitrification - Reactor No. 5.

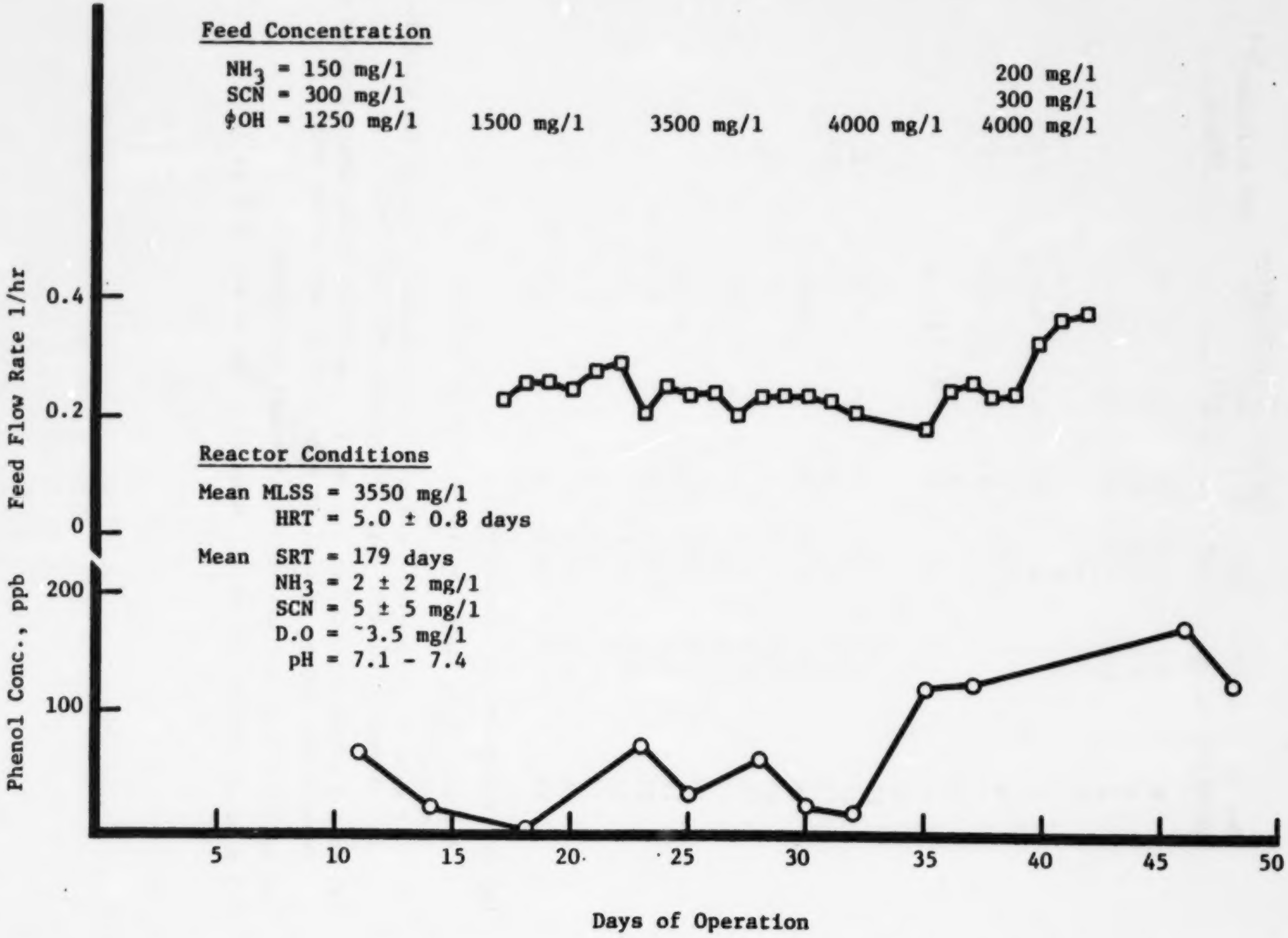
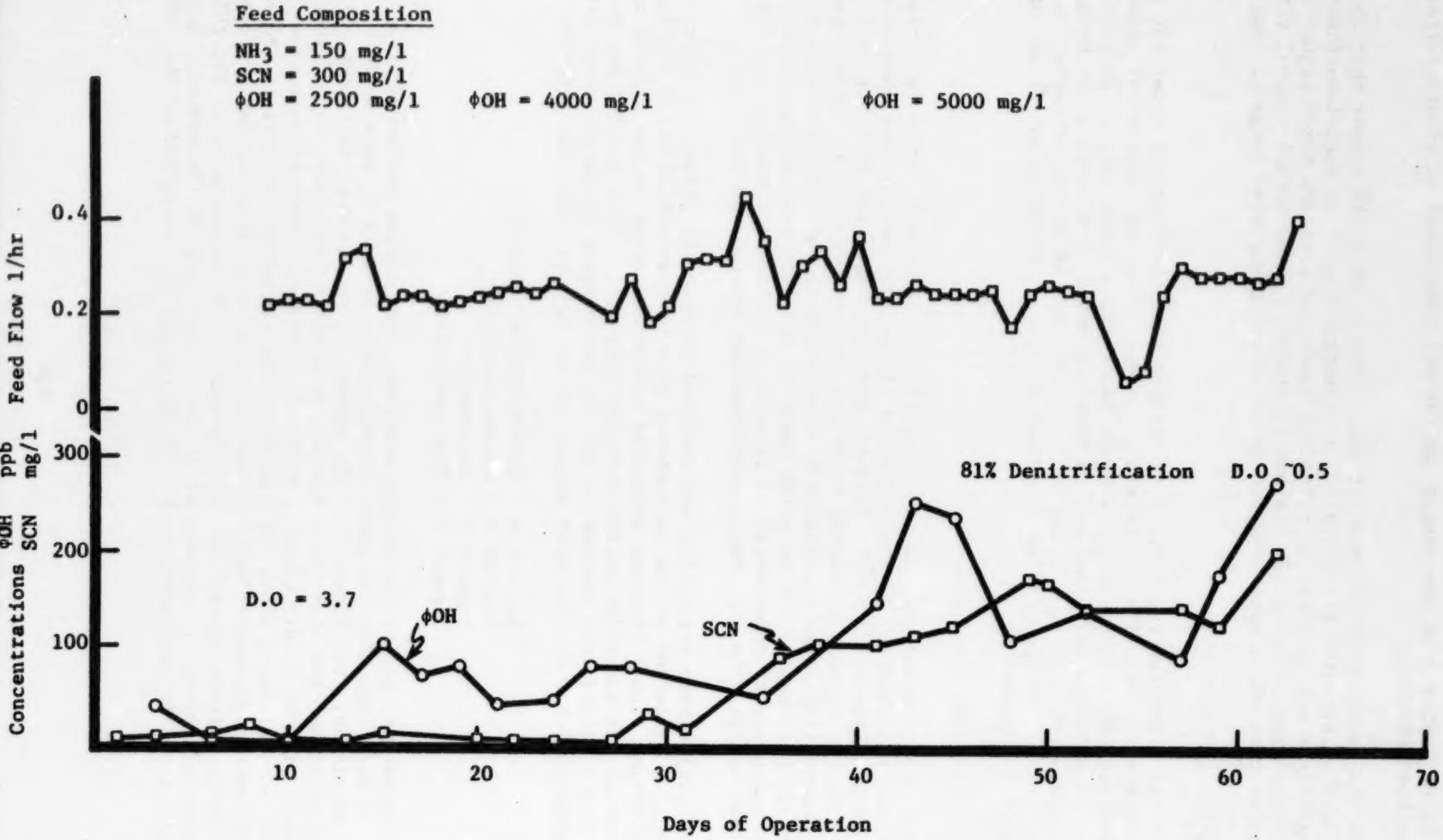


Figure 21. Effect of High Feed Phenol Concentration on Nitrification in Reactor No. 6.



would be washed from the reactor and in all likelihood an adverse effect would have been observed.

From the observations on reactor nos. 5 and 6, it would appear that the key factors maintaining nitrification in situations of high phenol wastewater concentrations are long sludge retention times and adequate mixed liquor dissolved oxygen. Throughout the entire study program, phenol removal efficiencies greater than 99.9% were achieved under an extremely wide range of conditions.

PROCESS ENHANCEMENT

From the preceding section, it is evident that the reaction rates for the nitrification reaction are relatively slow. Thus, any economical means of enhancing these reaction rates would be of significant value. In this program three approaches were examined as possible modes of enhancing the phenol-nitrification process. These are: 1) addition of activated carbon to the reactor, 2) the application of mutant strains of bacteria and 3) carbonate nutrient supplement.

Activated Carbon Addition

There are numerous reports on the ability of activated carbon to extend or enhance the capacity of the activated sludge treatment system when added to the mixed liquor.(3, 4, 5) Further, with impending BAT effluent limitations on priority organic compounds there was the potential of the added benefit of controlling these pollutants by simply adding controlled amounts of activated carbon to the aeration basin of the activated sludge process. With the prospects of these benefits in mind, a preliminary evaluation of activated carbon addition to the phenol-nitrification process was undertaken.

This preliminary evaluation was designed to test the effects of a one time addition of carbon on the performance of a phenol-nitrification reactor. Sufficient finely grounded activated carbon was added to the reactor to increase the suspended solids level by 1400 mg/l. This reactor was operated with a standard feed wastewater and the performance characteristics are presented in Table 7. The test period can be divided into four segments -

Segment A - Before carbon addition
Segment B - Carbon addition
Segment C - Acclimation
Segment D - True evaluation

In segment A, before the carbon addition, the reactor performed at a k_A rate of 78 mg/l/day. For the mixed liquor sludge used, a k_A rate of 80 mg/l/day is predicted, (see Figure 5). In segment B, immediately following the carbon addition, the observed oxidation rate was 85 mg/l/day, well within the limits of that predicted and previously observed. However, after seventeen days of operation, about day 23, there was a gradual increase in the reactor thiocyanate concentration; an event which covered about 15 days. From the data in Table 7 there appears to be no reason for this excursion in the thiocyanate reaction. Also, it appeared as if the effort to push the reactor, days 20 through 26, by increasing the feed flow could have resulted in the increased

Table 7. PERFORMANCE OF REACTOR NO. 5 WITH 1400 mg/l ACTIVATED CARBON ADDED TO THE MIXED LIQUOR(a)

	Reactor Conditions and Concentrations					
Day of Operation	pH	HRT, Days	DO mg/l	NH_3 mg/l	SCN mg/l	ϕOH µg/l
0	7.3	3.3	3	12	4	22
1	7.1	2.9	4	-		
2	7.3	2.3	4	-		
3	7.0	2.6	4	0	4	3
4	7.0	2.7	2	32		
5	7.0	2.8	3	3	2	0
6	7.1	2.5	3	18		
		2.7 ± 0.3		13 ± 11	3	8
7	7.6	2.7	3	0	2	0
8		2.8		6	2	0
9		3.2		0	2	0
10		2.3		0	1	0
11		2.4		14	2	0
12		2.1		0	2	4
13		4.3		0		
14		2.8		0	0	0
15		3.4		-		
16				-		
17		2.8		1	2	0
18	7.3	2.6	6	0		
19	7.1	2.4	6	1	3	20
20	7.6	1.8	3	1		
21	7.5	1.6	3	9	2	13
22	7.4	1.8	5	-		
23	7.6	2.6	5	-		
		2.6 ± 0.7				
24	7.5	2.9	3	44	20	16
25	7.5	1.7	3	20		
26	7.4	1.7	3	6	25	41
27	7.2	4.3	2	9		
28	7.5	1.9	6	12	12	34
29	7.4	5.1	4	-		
30	7.5	5.5	4	3		
31	7.4	5.8	4	2	103	13
32	7.2	-	3	4	67	56
33	7.2	11.6	5	8		
34	7.3	5.7	5	8	81	7
35	7.2	5.4	5	-		
36	7.2	5.0	5	-		
37	7.2	4.3	5	6	81	0
38	7.2	4.4	3	3	47	71
39	7.2	4.2	5	10	0	52

Average Solids
TVS = 4300 mg/l
VSS = 4247 mg/l
SS = 4430 mg/l
k = 78 mg/l/day

Activated Carbon Addition to 1400 mg/l SS on day 7

k = 85 mg/l/day

Table 7. PERFORMANCE OF REACTOR NO. 5 WITH 1400 mg/l ACTIVATED CARBON ADDED TO THE MIXED LIQUOR$^{(a)}$ (CONTINUED)

	Reactor Conditions and Concentrations						
Day of Operation	pH	HRT, Days	DO mg/l	NH_3 mg/l	SCN mg/l	ϕOH μg/l	
40	7.2	4.3	5	7	0	34	
41	7.1	4.4	4	-			
42	7.2	4.6	5	-			
43	7.3	2.6	5	10	9	41	
44	7.5	4.1	5	0	3	80	
45	7.2	3.9	4	0	5	10	
46	7.2	3.9	4	0	5	0	
47	7.2	5.1	4	2	3	0	
48	7.2	4.6	4	-			
49	7.2	4.9	4	3	0	0	
50	7.2	4.4	4	11	0	0	
51	7.2	4.8	3	0	0	0	
52	7.2	4.3	4	2	0	0	
53	7.2	4.0	2	1	0		
54	7.1	4.3	5	-			
55	7.2	4.4	5	-			
56	7.2	6.5	5	7			
57		7.9		9	7	84	
58	7.2	4.8	5	9			
59	7.2	4.1	3	9	5	30	
60	7.2	3.3	5	-			
61	7.2	3.4	5	-			
62	7.2	2.9	5	3	1	128	
63	7.3	3.6	5	9			
64	7.3	3.8	4	9	0	41	
65	7.3	2.8	5	9			
66	7.3	2.4	4	3	3	37	
67	7.4	1.5	6	9	0	0	
68	7.1	1.9	5				
69	7.3	1.7	2	2	0	10	
70	6.9	1.6	2	12			
71	6.9	1.6	5	13	3	3	
72	7.6	1.4	1	0	4	10	
73	8.0	1.7	1	2	19	27	
74	7.9	1.6	2	4	92	34	high pH
75	7.9	1.5	2	11	125	10	
76	7.8	-	5	0	5	13	
77	7.4	-	4	1			
78	7.3	1.9	3	7	6	0	
79	7.2	1.7	4	0			
80	6.8	1.4	4				
81	6.6	1.5	3	4	0	23	
82	7.1	1.5	4	5	21	23	
83	7.0	1.6	0.6	4			

Table 7. PERFORMANCE OF REACTOR NO. 5 WITH 1400 mg/l ACTIVATED CARBON ADDED TO THE MIXED LIQUOR(a) (CONTINUED)

	Reactor Conditions and Concentrations						
Day of Operation	pH	HRT, Days	DO mg/l	NH_3 mg/l	SCN mg/l	φOH μg/l	
84	7.4	1.6	0.8	3	6	0	
85	7.6	1.7	0.6	62			
86	7.5	1.7	0.6	78			low DO
87	7.7	1.7	0.6	99			
88	6.5	-	2.2	15		0	
89	6.8	1.5	0.8	35			
90	6.5	1.3	0.4	54	0	16	low DO
91	6.5	1.4	6	31			
92	6.5	1.4	4	26	0	0	
93	6.9	1.2	3	0			
94	7.3	0.9	4	0			
95	7.5	1.9	5	0	7	23	
96	7.4	1.3	4	0	1		
97	7.4	1.4	5	0	7		
98	6.6	1.8	5	13			
99	6.6	1.9	3	16			k = 136 mg/l/day
100	7.1	1.3	5	3			
101	7.1	1.5	5	0	5	0	
		1.6 ± 0.2		6 ± 8(b)	4 ± 5(c,d)		

(a) Reactor temperature 79-88°F
Feed to reactor: ·NH_3 = 150 mg/l
·SCN = 300 mg/l
·φOH = 500 mg/l

(b) Values on days 85-88 and 89 and 90 omitted.

(c) Values on days 73 to 75 omitted.

(d) Negative numbers observed due to variability of actual numbers.

ammonia concentrations. A possible explanation is that the carbon might have gleaned out trace quantities of toxic or inhibitory materials from the wastewater thus creating an environment of relatively high levels of these toxic/inhibitory materials. The results were ammonia and thiocyanate excursions, and the need to re-acclimate the sludge.

Following this acclimation period, the reactor was once again pushed and in segment D it can be seen that high levels of treatment were achieved. There were a few accountable excursions. Nevertheless, the oxidation rate was much higher than that previously observed, k_A of 136 mg/l/day. It is not conclusive that this increased oxidation rate was due to the carbon because no effort was made in the course of this experiment to determine the amount of new sludge formed. Further, in previous experiments it was observed that the biological sludges used can be pushed to produce much higher oxidation rates than those predicted by the correlation shown in Figure 5 (k_A = 15.2 TVS mg/l/day).

From the above data, the ability of the activated carbon to enhance the biological reaction when added to the mixed liquor remains unconfirmed and should be re-examined.

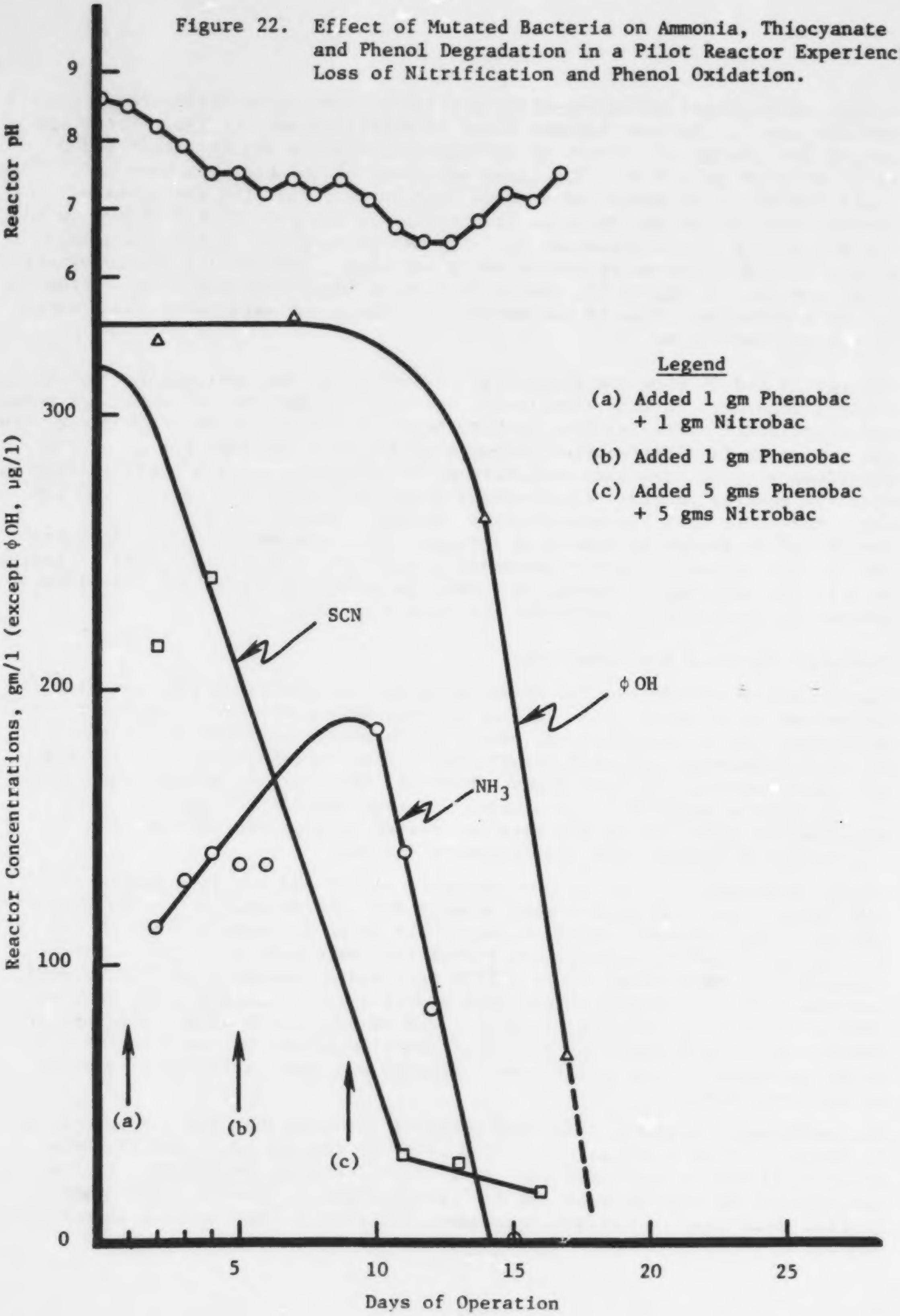
The addition of activated carbon to the experimental reactors did produce other positive effects, these include: 1) the elimination of foaming in the reactor, 2) improved settleability of the sludge and 3) significant improvement in the color of the effluent from a definite brown to a pale straw color. Analysis for priority organic pollutant control showed that the activated carbon addition to the mixed liquor did not produce any better control than other reactors which operated without carbon. This observation must be qualified by the facts that (a) carbon addition to the reactor was a one-time addition and (b) the sample analyzed was taken after 1055 l of wastewater had been treated over an operating period of 103 days. These conditions could have been well beyond the breakthrough point for the carbon used. The impact of the priority pollutants regulations and the potential of this mode of operation as a control technology are more reasons for another examination of carbon addition to the mixed liquor.

Application of Commercially Available Mutant Bacteria

In the preliminary studies which lead up to the present program, the experience after an upset was a lengthy time consuming effort to re-establish nitrification in the test reactor. One of the goals of this program is to develop an understanding of the process such that more effective corrective measures could be taken in the event of an upset. However, it was also felt that other means of accelerating the recovery would be beneficial. Certain suppliers of mutant strains of bacteria claim their products are capable of accelerating the recovery of biological treatment systems that are experiencing problems. Thus it was decided to test two mutant strains -- a "hydrocarbon degrader" and an "ammonia recoverer."

These organisms were tested in a combined dose at rates recommended by the supplier. The mixture was added to a reactor in which nitrification activity was disrupted and the data in Figure 22 show the chronology of events. On the basis of the present understanding of the biological process involved in the

Figure 22. Effect of Mutated Bacteria on Ammonia, Thiocyanate and Phenol Degradation in a Pilot Reactor Experiencing Loss of Nitrification and Phenol Oxidation.



single stage phenol oxidation-nitrification of coke plant wastewater, it appears that the initial failure (loss of nitrification) of the reactor was due to the synergistic effect of the high thiocyanate concentration (>300 mg/l) and high pH (~8.6). The three additions of the bacteria show no immediate effect on phenol or ammonia. It appears that the thiocyanate response was due to the increase in activity as a result of the change in pH, and the return of nitrification activity was in response to the inhibitory stress of high thiocyanate and pH being relieved. The results of the experiment, the data in Figure 22, appear to show no real clear cut benefit from the bacteria addition. Thus it was decided to repeat the experiment under more controlled conditions.

Figures 23 and 24 show the chronology of events for the test reactor and a control reactor. In this experiment, there were rapid responses to high phenol and thiocyanate concentrations in both test and control reactors. However, there was a more rapid nitrification response in the test reactor; but in earlier experiments there were also observations of unexpectedly high nitrification rates when the reactor received high ammonia loadings. Thus, the indications are still not clear that the commercially available mutant bacteria will be beneficial in producing immediate recovery from an upset episode. However, the results are sufficiently interesting that this possibility could be applied on a hit or miss understanding or a more detailed and controlled experimental program be conducted to delineate the true potential.

Carbonate Nutrient Supplementation

The organisms responsible for thiocyanate and sulfide oxidation, and nitrification are autotrophs. They utilize carbonate as their carbon source in cell synthesis. It is generally believed that carbonate supplied by the activity of the heterotrophs and that solubilized during aeration would satisfy the carbonate needs of the autotrophs. However, there was no supporting evidence in the reports reviewed. Consequently, a test reactor was operated with supplemental carbonate in the feed wastewater to test the premise that the autotrophic reactions were not carbonate limited.

Sodium carbonate was used as the carbonate source and not as a source of alkalinity. The feed to the test reactor was supplemented with 1000 mg/l of Na_2CO_3. This carbonate addition did result in an increase in both pH and alkalinity. However, appropriate corrections were made to maintain the standard feed alkalinity of about 1000 mg/l and a reactor pH of 7.2 by acid addition. It is recognized that acid addition would liberate some of the carbonates as CO_2. However, both the feed pH and the pH of the reactors are maintained sufficiently high such that the bicarbonate pH end-point of 6.5 is not exceeded. Thus, while some carbonate was lost, sufficient remained to test the premise.

The performance data for this experiment is shown as that for reactor no. 4 in Table 2. From a comparison of the data for reactor no. 4 and the other reactors it can be concluded that sufficient carbonate is supplied by the activity of the heterotrophs and through aeration to prevent a carbonate limited condition. In effect, carbonate addition did not enhance autotrophic activity.

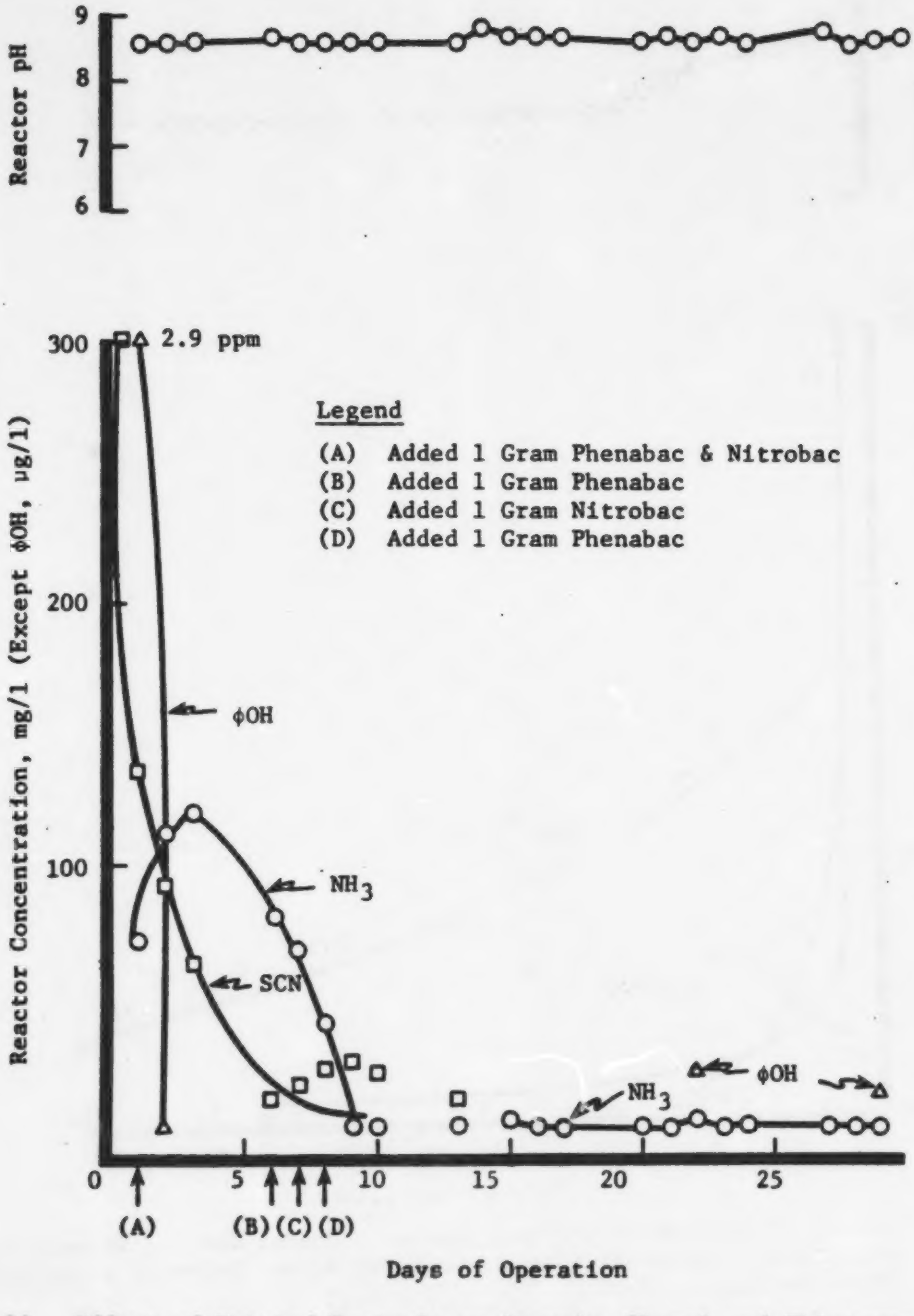


Figure 23. Effect of Mutated Bacteria on Ammonia, Phenol and Thiocyanate Degradation at a pH of 8.6.

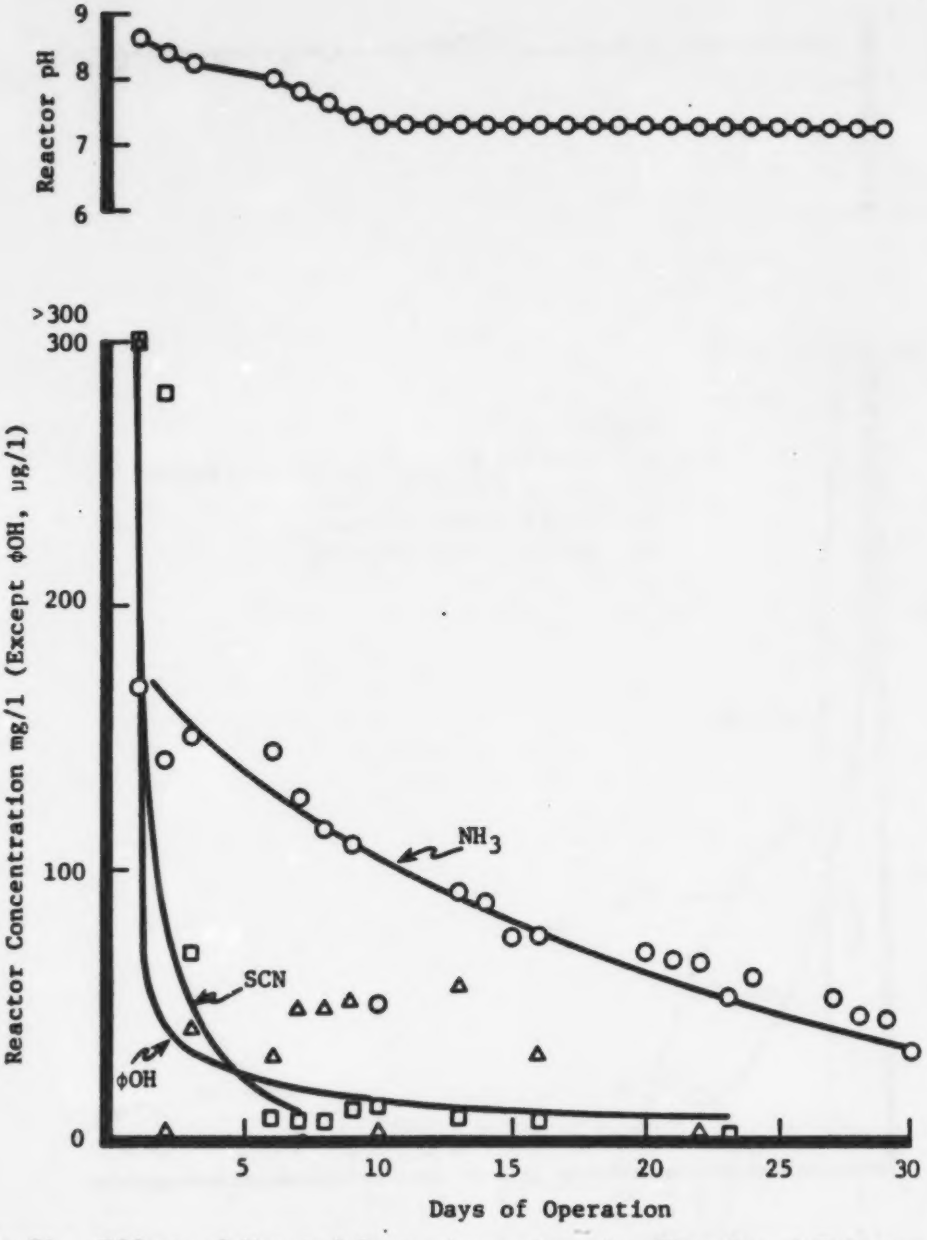


Figure 24. Effect of Mutated Bacteria on Ammonia, Phenol and Thiocyanate Degradation Corresponding to Control for Mutant Bacteria Experiment Shown on Figure 23.

CONTROL OF PRIORITY ORGANIC POLLUTANTS

Thirteen grab samples were taken for gas chromatograph/mass spectrograph, GC/MS, analysis in an effort to determine the fate of priority organic pollutants in the course of the treatment of coke plant wastewaters. The treatment train under consideration is shown in Figure 25. Each sample was prepared and handled in accordance with the EPA specified protocol. The analysis examined 78 organic compounds covering the range of purgables (volatiles), base/neutrals and acid extractables. This discussion will be directed at only those compounds which were detected.

The thirteen samples analyzed covered two treatment schemes:

- A conventional phenol biological reactor (Weirton Steel's Brown's Island Coke Plant), and
- An advanced single-stage phenol-nitrification biological treatment.

Table 8 presents the analytical data for the conventional phenol biological reactor scenario. This data strongly suggest a significant reduction in the purgables as the wastewater traversed the ammonia still. However, higher concentrations of purgables appear in the bio-plant effluent. Overall there were lower concentrations of priority organic compounds in the bio-plant effluent than the ammonia still waste entering the plant, especially the base neutrals and acid extractables.

Table 9 presents the data for the advanced single stage scenario, more precisely treatment across a phenol-nitrification activated sludge reactor. This data also show an overall decrease in the concentrations of the priority organic compounds. On the average, the concentration of the compound detected was less than 10 μg/l. There was only one exception, methylene chloride. Further, the concentrations observed in the effluent from the experimental bio-reactors were much lower than that from the Brown's Island plant.

In evaluating the data in Table 9 it is apparent that the effluent qualities from the different reactors are all about equivalent. However, it must be recognized that reactor no. 5 dated November 13, 1979 was operated with activiated carbon added to the mixed liquor. It appears that the carbon addition did not improve the quality of the treated effluent relative to controlling the priority organic pollutants. This observation should not be viewed as being totally negative because it must be noted that the carbon addition was a one-time addition and the effluent sample for GC/MS analysis was taken after about 1055 liters of wastewater had been treated over a 103 day period. It is very likely that after this extended service that the adsorptive capacity of the carbon might have been exhausted.

In a comparison of the phenol values determined by the GC/MS procedure and the Standard Methods wet chemistry procedure, there were significant discrepancies, as shown in Table 10. Three major factors are believed to be responsible for these discrepancies. The first factor is the fact that several phenols, other

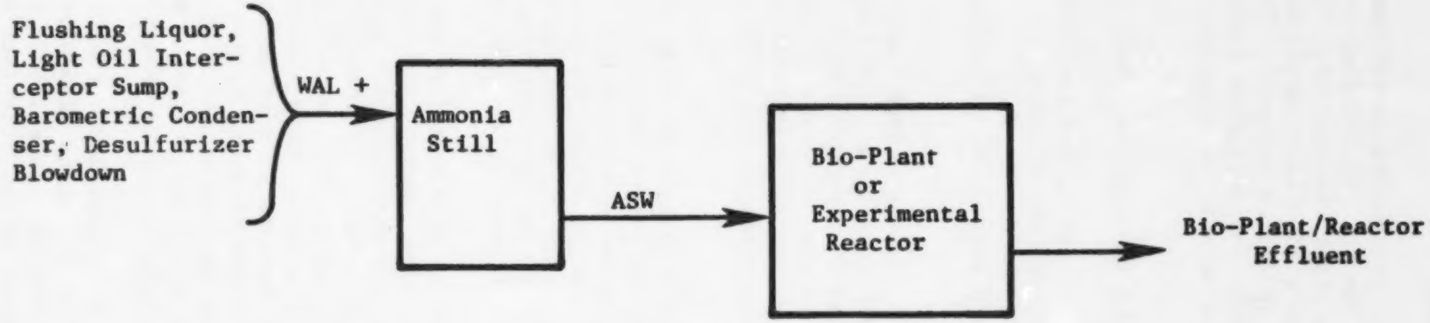

Flushing Liquor, Light Oil Interceptor Sump, Barometric Condenser, Desulfurizer Blowdown
WAL +
Ammonia Still
ASW
Bio-Plant or Experimental Reactor
Bio-Plant/Reactor Effluent

Figure 25. Treatment Train for By-Product Coke Plant Wastewater under Consideration for Effect on Priority Organic Pollutants.

Table 8. PRIORITY ORGANIC POLLUTANT PROFILE THROUGH THE WEIRTON STEEL BROWN'S ISLAND COKE PLANT WASTEWATER TREATMENT SYSTEM

Sample Source	WAL(a)	ASW(b)	ASW	Bio Plant Effluent(c)	Bio Plant Effluent(c)
Date	11/7/79	9/15/79	11/7/79	9/14/79	11/12/79
Compound		(all concentrations in μg/l)			
Purgables					
methylene chloride	210.73	0.53	48.52	0.41	310.22
1,1-dichloroethane	ND(d)	0.24	ND	0.16	ND
chloroform	2.26	7.81	ND	11.48	5.82
1,1,1-trichloroethane	185.21	3.92	ND	3.78	302.82
benzene	4,507.34	2.35	257.88	0.25	17.01
toluene	960.89	ND	ND	ND	7.00
Base Neutrals					
bis(2-chloroethoxy)methane	ND	125.64	ND	ND	ND
naphthalene	6,356.25	30.24	14.51	1.00	ND
acenaphthalene	449.34	38.52	ND	2.21	10.56
acenaphthene	ND	41.40	ND	ND	ND
diethylphthalate	31.59	64.11	ND	5.39	ND
1,2-diphenylhydrazine	ND	23.76	ND	0.34	ND
N-nitrosodiphenylamine	ND	48.30	ND	2.95	ND
phenanthrene anthracene	ND	12.34	ND	3.04	ND
di-n-butylphthalate	ND	632.88	ND	23.63	ND
fluoranthene	324.70	261.33	1,038.00	13.29	210.71
pyrene	312.38	418.20	837.76	28.06	210.57
benzo(a)anthracene chrysene	ND	1,591.80	525.70	85.54	421.74
butylbenzylphthalate	58.22	ND	ND	ND	ND
benzo(b)fluoranthene benzo(k)fluoranthene	ND	ND	236.32	ND	276.48
benzo(a)pyrene	ND	ND	441.90	ND	744.19
Acid Extractables					
phenol	12,073.50	97,834.80	21,897.44	ND	1.02
2,4-dimethylphenol	ND	302.35	ND	0.01	ND

(a) All wastewaters (flushing liquor, light oil interceptor scrap, barometric condenser, and desulfurize blowdown) collected together for processing through an ammonia still.

(b) Feed to bio-plant, normal operation of ammonia still (consistent with present discharge permits).

(c) Brown's Island operating conditions: MLSS ~1000 mg/l; HRT ~2.2 days; SRT ~5-10 days.

(d) Analyzed for but not detected.

Table 9. PRIORITY ORGANIC POLLUTANT PROFILE THROUGH PHENOL-NITRIFICATION BENCH SCALE ACTIVATED SLUDGE REACTORS TREATING COKE PLANT WASTEWATER

Sample Source	No. 2 Feed	ASW(a)	No. 1&5 Feed(b)	No. 1 Effluent	No. 5 Effluent	No. 2 Effluent	No. 8 Effluent	No. 5 Effluent(c)
Date	8/23/79	11/7/79	9/14/79	9/19/79	9/19/79	11/12/79	11/12/79	11/13/79
Compounds				(all concentrations in μg/l)				
Purgables								
methylene chloride	5.14	5.78	1.91	71.28	75.75	417.18	5.43	4.21
1,1-dichloroethane	ND(d)	ND	ND	ND	ND	ND	ND	ND
chloroform	8.54	1.92	0.43	1.18	0.43	6.38	3.28	1.00
1,1,1-trichloroethane	2.17	8.67	2.64	2.81	1.48	ND	11.00	17.90
benzene	0.37	18.78	1.01	0.17	0.17	8.42	6.60	10.70
toluene	ND	ND	ND	ND	ND	ND	ND	ND
Base Neutrals								
bis(2-chloroethoxy)methane	ND	ND	467.76	ND	ND	ND	ND	ND
naphthalene	ND	ND	ND	ND	2.14	0.19	ND	ND
acenaphthalene	93.14	43.38	37.26	ND	4.09	0.23	0.57	0.22
diethylphthalate	66.13	ND	161.46	0.28	0.53	ND	ND	ND
1,2-diphenylhydrazine	ND	ND	5.99	ND	ND	ND	ND	ND
N-nitrosodiphenylamine	213.44	ND	ND	0.35	ND	0.98	ND	ND
phenanthrene								
anthracene	ND	ND	31.95	ND	ND	ND	ND	ND
di-n-butylphthalate	502.16	ND	869.52	2.47	8.98	1.15	0.87	0.41
fluoranthene	467.19	528.86	152.55	0.22	1.74	35.18	3.48	3.46
pyrene	527.00	462.84	162.69	0.33	1.64	ND	3.07	1.95
benzo(a)anthracene chrysene	1,310.23	560.58	457.02	ND	ND	2.70	6.65	5.58
butylbenzylphthalate	ND	ND	ND	ND	ND	1.03	ND	ND
benzo(b)fluoranthene benzo(k)fluoranthene	ND	242.59	ND	ND	ND	2.28	3.86	0.87
benzo(a)pyrene	ND	1,716.34	ND	ND	ND	10.16	7.67	7.80
acenaphthene	ND	ND	ND	ND	0.32	ND	ND	ND
Acid Extractables								
phenol	60,378.00	32,249.32	65,820.00	0.56	0.08	0.84	0.15	0.23
2,4-dimethylphenol	174.91	255.04	256.34	ND	ND	ND	ND	ND

(a) Ammonia still operated to produce low ammonia concentration, <150 mg/l. This ASW subsequently amended with ammonia, phenol, thiocyanate and other components as required; this amended ASW was used as feed to experimental reactors.

(b) Same as (a) but used in the preparation of feed to reactors nos. 1 and 5.

(c) Reactor 5 operated with activated carbon added to the mixed liquor.

(d) Analyzed for but not detected.

Table 10. COMPARISON OF TOTAL PHENOL VALUES DETERMINED BY GC/MS AND STANDARD METHODS PROCEDURES

Sample	Total Phenol Concentration, μg/l GC/MS	Standard Methods
ASW Feed to BI-Bio Plant, 9/14/79	98,000	280,700
WAL + (Charge to Ammonia Still), 11/7/79	12,244	207,400
ASW Feed to BI-Bio Plant, 11/7/79	21,897	176,600
ASW (Still Operated for Low NH_3), 11/7/79	32,504	193,000
BI-Bio Plant Effluent, 9/14/79	0.13	34
BI-Bio Plant Effluent, 11/12/79	1.02	52
ASW* (Still Operated for Low NH_3) Feed for Reactor Nos. 1 & 5 Before Alteration	66,000	268,000
Feed ASW to Reactor No. 2, 8/23/79	61,000	500,000
Effluent from Reactor No. 1, 9/19/79	0.66	ND(a)
Effluent from Reactor No. 5, 9/19/79	2.44	ND
Effluent from Reactor No. 2	0.84	ND
Effluent from Reactor No. 8, 11/12/79	0.15	ND
Effluent from Reactor No. 5, 11/13/79	0.25	ND

(a) Not detectable.

than those measured by GC/MS, are present in the wastewater. The second more important factor is the relatively poor solvent extraction efficiencies for such materials when applying the EPA protocol. The third factor, which is probably the most troubling, is the observation of "crossover" of extractables, i.e., acid extractables compounds were found in the base neutral extraction and vice versa. The severity of this "crossover" appeared to vary from sample to sample but was most severe with the high concentration samples. The problem of extraction efficiency is not limited to the phenols only. Stamoudix et al(6) demonstrated poor extraction efficiencies for several compounds in single component systems using the EPA extraction protocol; data reproduced in Table 11.

Table 11. RECOVERY EFFICIENCIES FOR DIFFERENT ORGANIC COMPOUNDS EXTRACTED FROM SPIKED DISTILLED WATER (DATA OF STAMOUDIS ET AL)

Compound Name	% Recovery
O-xylene	42
3-octanone	71
1-heptanol	70
n-butylbenzene	32
phenol	61
cresol	75
o-ethylphenol	105
d_{10}-anthracene	133

SUMMARY AND CONCLUSIONS

It is anticipated that the Federal government will issue Best Available Technology Economically Achievable (BAT) limitations that will severely limit the discharge of ammonia, sulfides, cyanides, phenol and priority pollutants in coke plant wastewater discharges. Preliminary indications are that the technology to meet the limitations will be staged biological treatment followed by alkaline chlorination and filtration or activated carbon adsorption followed by alkaline chlorination and filtration. A study of a single stage phenol-nitrification process for the treatment of coke plant wastewaters was undertaken to evaluate its potential as an alternative to either stage biological treatment or activiated carbon technology. Objectives of the single stage phenol-nitrification process study were:

1. To determine the operating conditions necessary to achieve an effluent of 10 ppm or less of ammonia and measure the corresponding concentration of other pollutants;

2. To determine the effect (inhibitory) of certain constituent compounds and ions in coke plant waters;

3. To conduct preliminary examination of methods for enhancing the operation of the process;

4. To determine the effect of the process on priority organic pollutants in coke plant waters and

5. To develop a better understanding of the different reactions and interactions, operation of and performance of the process.

The study was essentially a laboratory investigation in which actual coke plant wastewaters were examined. In addition, in evaluating the biological degradation of priority organic pollutants, a set of samples was taken from an existing industrial facility which represented a current Best Practical Treatment (BPT) facility. Water used in the laboratory work was an actual coke plant wastewater that was chemically adjusted as needed for the study.

The specific conclusions from the study are:

1. The single stage phenol-nitrification process has the potential of producing an effluent concentration of NH_3 = 10 mg/l, total cyanides = 10-110 mg/l; phenols = <200 µg/l; and sulfide = 0.5 mg/l from ammonia stripped undiluted coke plant wastewater.

2. Typical required operating conditions:

    a. Detention Time - 3 days
    b. Biomass Concentration - 2-3 grams per liter
    c. Dissolved Oxygen - Above 1.5 mg/l
    d. Temperature - $80^{\circ}F$
    e. pH - 7.0 to 7.7

3. The process is effective in the degradation of organic priority pollutants. Major factors that influence the degree of priority pollutant degradation are hydraulic and sludge residence time. Longer residence time improves removal.

4. The process is very effective upon free cyanides but ineffective upon complex cyanides.

5. The rate of nitrogen oxidation observed in the control reactors was in agreement with the correlation

$$k_A = 15.2 \text{ TVS, mg/l/day}$$

where TVS = mixed liquor total volatile solids, g/l. Sludge growth was determined, Y_{max} of 0.7 mg SS/mg N oxidized; biological maintenance energy utilization rate, b, of 0.004 day^{-1}.

6. Optimum pH condition for the phenol-nitrification process is in the range of 7.0-7.7 with the temperature range being $80\text{-}90^{\circ}F$.

7. Alkalinity requirements are 4-5 mg as $CaCO_3$ per mg of nitrogen oxidized.

8. Sudden nitrogen loading increases to the reactor can be tolerated for reasonable periods of time provided reactor conditions, especially pH and DO,

are maintained at near optimum conditions without severe disruption of biological activity. It must be noted that the effluent quality may change, i.e., ammonia concentrations may increase.

9. A 67% increase in thiocyanate loading did not affect nitrification.

10. Thiocyanate concentrations up to 150 mg/l in the reactor did not disrupt the nitrification process but a synergistic effect between thiocyanate concentration and pH greater than 8.0 did produce inhibition at lower concentrations.

11. Reactor pH's greater than 8.0 noticeably inhibited thiocyanate degradation.

12. Free cyanide severely inhibited nitrification, but the nitrifying organisms were capable of acclimating to concentrations up to 12.0 mg/l free cyanide.

13. Free cyanide concentration up to 12 mg/l did not affect the thiocyanate organisms.

14. Complex cyanide concentrations between 10-110 mg/l were found to pass through the biological process unaltered.

15. The direct addition of by-product light oil to the reactor in an amount up to 2000 mg/l did not appear to have any effect on the biological reactions. In practice this occurrence might affect the oxygen transfer and mixing ability of the aeration equipment.

16. Both direct addition of sulfide to the reactor to concentrations up to 40 mg/l and progressively increasing the sulfide loading rates to test reactors produced no adverse effects.

17. The nitrifying organisms were capable of acclimating to phenol concentrations in the reactor up to 30 mg/l.

18. Wastewater with phenol concentrations up to 5000 mg/l were effectively treated. Throughout the study, treated wastewater phenol concentrations were consistently less than the 0.5 mg/l BAT limit proposed (Alternate 1).

19. Process enhancement by the addition of activated carbon to the mixed liquor was not conclusive. Additions of activated carbon aesthetically improved the appearance of the effluent. It also appeared to enhance the settleability of suspended solids in the effluent.

20. In the treatment of coke plant wastewater, the autotrophic reactions are not carbonate limited.

21. The process was found to require close operator attention, close control of the environment within the reactor and reasonably constant loading rates.

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NITROGEN AND CONTAMINANT CONTROL OF COKE PLANT EFFLUENTS IN AN UPGRADED BIOLOGICAL SYSTEM

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ABSTRACT

Bench scale treatability studies were conducted to evaluate the performance of the single sludge pre-denitrification nitrification process configuration for nitrogen and contaminant control of coke plant effluents.

Complete nitrogen control was achieved provided wastewater dilution was practised or low levels of powdered activated carbon (PAC) were added to the bioreactors. The minimum aerobic SRT required to achieve complete nitrification at 20-24°C was 22 days. Operation at high system SRT (60 d) did not facilitate nitrification of undiluted wastewater. However at anoxic and aerobic HRT's of 0.5-1 and 1-3 days, respectively, complete nitrogen control and high levels of contaminant removal were effected in undiluted wastewater by maintaining a PAC level of 500 $mg \cdot L^{-1}$ in the reactors. The equivalent PAC feed concentrations ranged from 20 to 50 $mg \cdot L^{-1}$. The addition of PAC overcame *Nitrobacter* inhibition, which was evident in the treatment of both diluted and undiluted wastewater.

The organic carbon in the wastewater was used as the energy source for denitrification and no supplemental organic carbon was required to achieve complete denitrification provided the feed FOC/TKN ratio ≥ 3.5.

The fate of trace organics was monitored using GC/MS methodology. Enhanced trace organic removal was effected through PAC addition.

Parallel units operated with and without calcium indicated that up to 3000 $mg \cdot L^{-1}$ of dissolved calcium in the wastewater was not detrimental to biological activity. Analysis confirmed that calcium phosphate tetrabasic was precipitated discretely in the reactors. Phosphoric acid requirements increased 10-fold when calcium was present.

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NITROGEN AND CONTAMINANT CONTROL OF COKE PLANT EFFLUENTS IN AN UPGRADED BIOLOGICAL SYSTEM

INTRODUCTION

The complete mix activated sludge process is generally used for the treatment of coke plant wastewaters in North America. The oxidation of phenolics, cyanide, thiocyanate and sulphides is achieved but few full-scale facilities achieve nitrification and no bioplants currently practise complete nitrogen control. This study has sought to determine the process conditions by which nitrogen control can be achieved economically. Inherently, this requires an optimum balance between the nitrification and denitrification processes. Evaluation of full-scale industrial experience[3] and cost analysis data[15] led to the adoption of a single sludge pre-denitrification nitrification process configuration for further study. The cost saving advantages offered by this process are twofold; firstly, the supplemental carbon required for denitrification is minimised or eliminated by the presence of raw wastewater organic carbon and secondly, alkalinity requirements are greatly reduced by coupling the nitrification and denitrification processes.

Accordingly, bench-scale treatability studies were initiated at the Wastewater Technology Centre, Burlington, Ontario, to produce a non-acutely lethal (to rainbow trout) effluent low in nitrogen concentration. Reactors were operated from October 1978 to April 1980. This period may be conveniently divided into two phases, the first being concerned with startup and acclimation and the second, with the determination of process conditions required to achieve high levels of nitrogen removal from a full strength coke plant wastewater.

Wastewater was provided by Dominion Foundry and Steel Limited (Dofasco), Hamilton, Ontario. This comprised a mixture of limed ammonia still effluent and a light oil interceptor sump wastewater.

A U.S. EPA survey of steel industry effluents[10] reported the presence of 73 of the 129 priority pollutants. The level to which this technology was successful in removing trace contaminants was evaluated by GC/MS analysis. This analysis was extended beyond the EPA priority pollutant list to include those trace contaminants that are indigenous to coke plant wastewaters.

EXPERIMENTAL PROCEDURES

Three identical process trains, A, B and C, were operated in parallel. Figure 1 depicts the process sequence for each train; a complete mix anoxic reactor (D1), a complete mix aerobic reactor (D2), and an upflow clarifier.

Operating procedures for reactor control have been detailed previously[4]. Briefly, feed rates of 5 to 15 $L \cdot d^{-1}$ were selected, allowing ranges of nominal anoxic hydraulic retention time (HRT) from 0.5 to 1.0 day and nominal aerobic HRT's from 1.1 to 3.0 days to be effected. Mixed liquor was recycled from the clarifier to the anoxic reactor at a ratio of 8:1. Strict SRT control was maintained. Aerobic reactor pH and DO were controlled at 7.0 and 3.0 $mg \cdot L^{-1}$ respectively. Temperature in the reactors varied from 20 to 24°C. An effluent phosphorus residual was maintained by controlled phosphorus addition to the anoxic reactor.

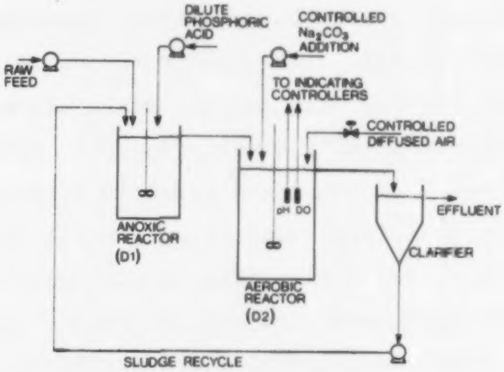


Figure 1, Process flow schmeatic.

ANALYTICAL PROCEDURES

Sample collection followed established protocol[4]. The filtered samples were analysed for conventional pollutants (Table 1) and trace organics according to previously reported procedures[4,5]. Sludge analysis by electron microscopy and x-ray diffraction has also been previously detailed[5]. Static 96-hr bioassays of the final effluents followed the EPS procedure for testing the acute lethality of liquid effluents to fish[9].

RESULTS AND DISCUSSION

Phase I

The seven-month initial phase incorporated startup and sludge acclimation, the objective being to establish fully equilibrated nitrifying systems. SRT was initially maintained at 60 to 70 days. Removal of 80% of the filtered organic carbon (FOC) and 99% phenol were quickly achieved but the systems were unstable with regard to nitrification and to oxidation of cyanide and thiocyanate. This behaviour was attributed to the wide variations in feed characteristics.

Pseudo-equilibrium conditions were subsequently achieved by controlling feed characteristics; raw feed was diluted 2:1 to 4:1 with tapwater and respiked with phenol, thiocyanate and methanol to achieve initial feed parameter concentrations. Values of equalized feed parameters are listed in Table 1. SRT values were then allowed to decline to a mean of approximately 30 days. Typical system operating parameters are summarized in Table 2 and typical effluent quality in Table 3.

Oxidation of carbonaceous material improved to 94% FOC removal and almost total phenol removal. The organic carbon requirements for the pre-denitrification systems were approximately twice the theoretical requirements confirming Sutton _et_ _al_'s observations[11]. Maintenance of the FOC/TKN level above a minimum of 3.5 ensured complete denitrification. This parameter is intimately associated with ammonia still operation. Excessively high ammonia levels in the still effluent will exceed the organic carbon availability in the wastewater and require carbon supplementation to maintain denitrification. This study showed that nitrification was sensitive to ammonia variability. In the early part of Phase I, this variation was four-fold before subsequent equalization reduced it to 1.6. Data from a full-scale plant treating a high-strength organic chemical wastewater[3] supports these findings; nitrification was achieved consistently provided the TKN_{max}/TKN_{mean} ratio ≤ 2.0. Equalization is not normally feasible in a steelworks environment since there is a constraint on land availability. However, efficient still operation can produce an effluent with approximately 100 $mg \cdot L^{-1}$ ammonia and thereby derive a three-fold cost saving since a greater amount of ammonia is recovered and neither carbon supplementation nor equalization are required.

Table 1, FEED CHARACTERISTICS - STEADY-STATE OPERATION, PHASE I

Parameter	Median $(mg \cdot L^{-1})$	95%* $(mg \cdot L^{-1})$	Variability**
FOC	470	570	1.21
Phenol	215	245	1.14
TKN	130	185	1.42
NH_3-N	75	120	1.60
TCN	1.0	1.6	1.60
CNS	170	180	1.06

* 95% of values were equal to or less than this value.
** 95% value divided by median.

Table 2, TYPICAL OPERATING CONDITIONS - PHASE I

Parameter	Anoxic Reactor (D1)	Aerobic Reactor (D2)	Clarifier Effluent
HRT (d)	1	3	
Temp (°C)	20- 24	22 - 24	
DO $(mg \cdot L^{-1})$	0.3	3.0	-
pH	7.5 - 8	7.0	-
TSS $(mg \cdot L^{-1})$	2000 - 2800	2000 - 2800	30
VSS $(mg \cdot L^{-1})$	1200 - 1500	1200 - 1500	20
OUR (d^{-1})	-	0.15 - 0.3	-
SVI $(mL \cdot g^{-1})$	-	50 - 100	-

Table 3, TYPICAL AEROBIC REACTOR EFFLUENT QUALITY - PHASE I
(SRT $\geq$30d at 20 to 24°C)

	FOC	Phenol	TKN	NH_3-N	NO_2-N	NO_3-N	TCN	CNS	TN*
Effluent $(mg \cdot L^{-1})$	30	0.050	5	<1	15	0	<1	<1	20
% Removal	94	>99.9	96	>99	-	-	~50	>99	85

* Total Nitrogen

The minimum SRT required to maintain nitrification (as measured by TKN disappearance) was identified as 30 days which equates to a minimum aerobic SRT of 22 days. All the oxidized nitrogen was completely denitrified. The absence of effluent NO_3-N indicated the inhibition of Nitrobacter by some specific trace contaminants in the coke plant wastewater. This phenomenon has been observed by other investigators[2,6]. Nevertheless, the 4:1 dilution of raw wastewater permitted nitrification and denitrification to proceed but was insufficient to prevent Nitrobacter inhibition.

Theoretical relationships indicate that 7.07 units of alkalinity as $CaCO_3$ are consumed per unit of NH_3-N nitrified and 3.57 units of alkalinity are generated per unit of NO_2-N or NO_3-N denitrified[12]. The stoichiometric net alkalinity requirement for the combined process can be estimated from the degree of nitrification and denitrification achieved. Approximately 50 to 60% of the alkalinity required in this system configuration was supplied via Na_2CO_3 addition (for pH control), the remaining requirement being satisfied by the residual alkalinity in the feed wastewater. On the basis of feed and effluent data in Tables 1 and 3, the alkalinity requirement was 2.38 g $CaCO_3$/gTN removed.

Fish bioassay tests were carried out to assess the toxicity of the effluent. The tests involved 96-h static bioassays using juvenile rainbow trout (Salmo gairdneri). Results indicated that the effluent was non-lethal, with zero mortality.

Phase II

The mode of equalization used in Phase I restored mean concentrations of the major pollutants, FOC, phenol and thiocyanate, by respiking, but diluted the level of trace contaminants. Ammonia variability was reduced which allowed nitrification to proceed as far as nitrite formation. Oxidation to nitrate did not occur since Nitrobacter growth was inhibited probably by the presence of the trace contaminants, albeit at low concentrations. Thus nitrogen control was achieved but the discharge of nitrite is environmentally unacceptable. In practice, to exercise nitrogen control by dilution and then discharge the nitrite would be an inappropriate procedure. Thus the main thrust of the treatability work was directed to defining the process conditions required to achieve high levels of nitrogen removal from a full strength coke plant wastewater.

Part 1 - Effect of Full-Strength Wastewater

Raw wastewater from Dofasco was used as received except that methanol was added as required to maintain the FOC/TKN ratio ≥3.5. Table 4 summarizes feed characteristics.

Table 4, FEED CHARACTERISTICS - PHASE II (PART 1)

Parameter	Median ($mg\cdot L^{-1}$)	95%* ($mg\cdot L^{-1}$)	Variability**
FOC	535	640	1.20
Phenol	185	269	1.45
TKN	155	214	1.38
NH_3-N	80	88	1.10
TCN	4.4	4.8	1.09
CNS	210	237	1.13

* 95% of values were equal to or less than this value.
** 95% value divided by median

At the start of Phase II, all three systems were operating at equilibrium SRT values between 30 and 35 days. Nitrification deteriorated significantly in all systems within two weeks of restoring the full strength feed; effluent ammonia concentration varied from 30 to 100 $mg\cdot L^{-1}$. This was not a satisfactory mode of operation.

Part 2 - Effect of PAC Addition

In order to re-establish nitrification, powdered activated carbon (PAC) was added to systems B and C at rates equivalent to 33 and 50 $mg\cdot L^{-1}$ in the feed. System A did not receive PAC, remaining as the "control". The resulting equilibrium reactor conditions are summarized in Table 5.

The feed characteristics for the remainder of the study are presented in Table 7. With the exception of organic carbon including phenol, the feed characteristics are very similar to those recorded earlier in the study. The feed organic carbon content increased steadily over the period that these data were averaged. Also, improved operation of the ammonia still reduced ammonia variability considerably below that experienced in the early part of Phase I.

Two weeks after PAC addition, System A remained unchanged whereas nitrification was reestablished in B and C. *Nitrobacter* inhibition had

Table 5, EQUILIBRIUM OPERATING CONDITIONS - PAC AND SRT EVALUATION

Reactor System		HRT (d)		SRT (d)	Average Reactor Solids ($mg\ L^{-1}$)			Equivalent PAC Feed ($mg \cdot L^{-1}$)	Clarifier Effluent VSS ($mg \cdot L^{-1}$)
		Anoxic	Aerobic		Biological MLVSS	MLSS	PAC		
Phase II Part 3	A	1	3	40	1780	2580	0	0	6
Phase II Part 2	A	1	3	60	2330	3880	0	0	7
	B	1	3	30	1920	3000	250	33	9
	C	1	3	40	2090	2750	500	50	8

Table 6, MEAN REACTOR EFFLUENT QUALITY - PAC AND SRT EVALUATION

Reactor System			Anoxic Reactor		Aerobic Reactor									
			FOC	NO_T-N*	FOC	Phenol	TKN	NH_3-N	NO_2-N	NO_3-N	TCN	CNS	ON	TN**
Phase II Part 3	A	Effluent***	-	-	31	0.034	72	68	4.0	0.0	3.4	1.1	-	76
		% Removal	-	-	94	>99.9	54	-	-	-	23	99.5	-	51
Phase II Part 2	A	Effluent	76	0.2	35	0.041	97	91	4.1	0.3	4.4	1.2	5.5	101.4
		% Removal	-	-	94	99.98	42	-	-	-	47	99.4	78	41
	B	Effluent	66	1.4	31	0.040	6	0.6	4.7	6.9	3.9	1.3	2.8	17.6
		% Removal	-	-	95	99.98	96.5	99.2	-	-	52	99.4	89	90
	C	Effluent	59	2.8	28	0.031	7	0.2	1.5	10.7	3.9	0.9	4.8	19.2
		% Removal	-	-	96	99.99	95.7	99.8	-	-	51	99.6	81	89

* Total oxidized nitrogen.
** Total nitrogen, TKN + NO_T-N.
*** Expressed in $mg \cdot L^{-1}$.

ceased since oxidation to nitrate had occurred. This trend continued to be observed over a 2-month period. Typical reactor effluent quality data are reported in Table 6.

Table 7, FEED CHARACTERISTICS - PHASE II (PARTS 2-5)

Parameter	Median	95%*	Variability**
FOC	680	810	1.19
Phenol	300	460	1.53
TKN	180	235	1.30
NH_3-N	88	120	1.36
TCN	8	24	3.00
CNS	240	355	1.48
ON***	25	62	2.48
pH	9.3	10.5	1.13

* 95% of the values were equal to or less than this value.

** 95% value divided by median.

*** Organic nitrogen, calculated as TKN-(NH_3-N)-(CNS-N)-(TCN-N).

Two sets of data are shown for system A in both Tables 5 and 6: the effect of high SRT was being examined concurrently in system A and so pertinent data is included in these tables although the effect is addressed in part 3. The data demonstrating the effect of PAC compares the three systems A, B, and C, during the second month of operation in this mode, under well-equilibrated conditions.

Effluent distribution data for TKN in Figure 2 shows that system A, the conventional pre-denitrification nitrification, could not nitrify full strength Dofasco wastewater confirming the observations in Part 1. Low levels of PAC addition in system B, enabled nitrification to proceed almost to completion. A higher nitrite concentration than in system C indicated that some minor inhibition of Nitrobacter had occurred. The higher level of PAC addition used in system C eliminated this inhibition and complete nitrification to nitrate was evident. Inhibition may have been due to the presence of one or more trace contaminants that were possibly adsorbed on to the PAC in systems B and C. Thiocyanate oxidation was achieved to the same degree in A, B and C (as was the oxidation of phenol and FOC) indicating that, in the case of coke plant wastewater, the nitrification process appears to be the most sensitive to inhibitory trace contaminants.

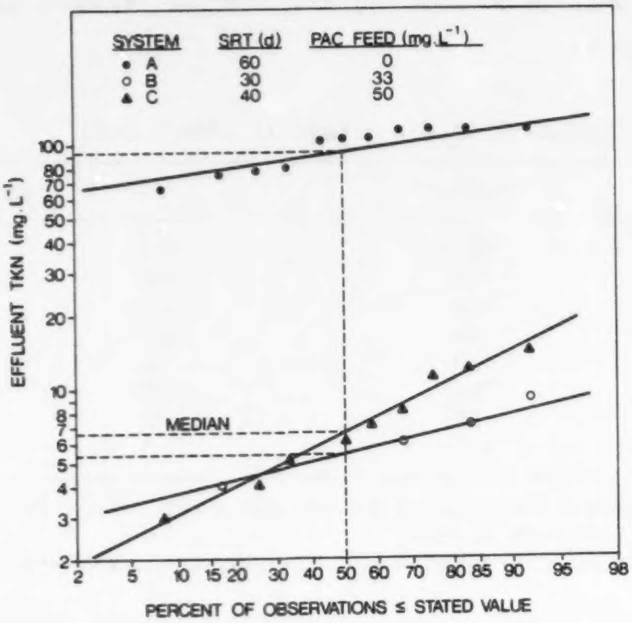


Figure 2, Effluent TKN data; PAC evaluation.

Part 3 - Effect of High SRT

Control data from system A during the PAC evaluation trials showed that nitrification of full strength wastewater could not be achieved at a system SRT of 40 days (Table 6). The system SRT was increased to an equilibrium level of 60 days to determine whether nitrification could be sustained at a higher SRT without PAC addition. A comparison of the effluent quality data for system A for both SRT values shows little change indicating that the single sludge pre-denitrification nitrification system was not capable of nitrifying full strength coke plant wastewater at elevated SRT values. Removal of FOC, phenol and thiocyanate remained unimpaired.

Part 4 - Effect of Calcium Precipitation

Most steel mills use combined free/fixed leg ammonia stills for the removal of ammonia. The most common alkali used for pH elevation in the fixed leg of the still is calcium hydroxide. As a result, the calcium content of limed weak ammonia liquor ranges from 1500 to 3000 $mg \cdot L^{-1}$. Observations made in Phase I[4] revealed precipitation of calcium in the reactors, with the result that the mixed liquor volatile fraction was reduced to less than 50%.

Other work[1,8] has attributed process instability to the formation of an inactive sludge caused by the precipitation of calcium carbonate. Consequently, parallel studies were conducted in Phase II to define the effect of precipitated calcium salts on the nitrification performance of the single sludge process configuration. To this end, two reactor systems were operated in parallel. System A was fed wastewater as received from Dofasco, containing between 1500 and ~2500 mg·L^{-1} of calcium. The feed to system C was carbonated at elevated pH to reduce the calcium content to levels always lower than 100 mg·L^{-1}. Both systems received PAC at a rate sufficient to maintain a reactor concentration of 500 mg·L^{-1}. The reactor systems were operated at steady state conditions (Table 8) for a four week period. The mean reactor effluent quality data for this period are shown in Table 9. They show no significant differences in nitrification performance and process stability (Figure 3). There was, however, an increase in effluent soluble organics in system C . This could be attributed to the lower adsorptive capacity of the lower PAC loading in the influent to system C .

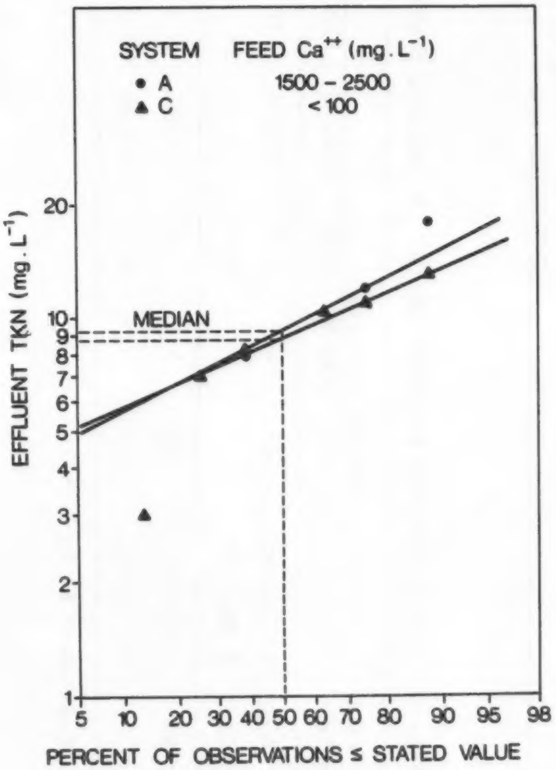


Figure 3, Effluent TKN data; effect of calcium.

Table 8, STEADY STATE OPERATING CONDITIONS - CALCIUM EFFECT

Reactor System	Feed Calcium ($mg \cdot L^{-1}$)	HRT (d)		SRT (d)	Average Reactor Solids ($mg \cdot L^{-1}$)			Equivalent PAC Feed ($mg \cdot L^{-1}$)	Clarifier Effluent VSS ($mg \cdot L^{-1}$)
		Anoxic	Aerobic		Biological MLVSS	MLSS	PAC		
A	1500 - 2500	1	3	40	2680	7230	500	50	12
C	<100	1	2	40	2900	4100	500	33	10

Table 9, MEAN REACTOR EFFLUENT QUALITY - CALCIUM EFFECT

Reactor System		Anoxic Reactor		Aerobic Reactor									
		FOC	NO_T-N	FOC	Phenol	TKN	NH_3-N	NO_2-N	NO_3-N	TCN	CNS	ON	TN
A	Effluent*	83	4.7	38	0.076	10	0.9	2.5	21.2	4.5	1.2	4.4	33.7
	% Removal	-	-	94.6	99.98	94.3	99.0	-	-	49	99.5	82	81
C	Effluent	81	5.7	47	0.086	9	0.7	2.4	13.3	6.3	2.1	4.2	24.7
	% Removal	-	-	93.4	99.98	95.1	99.1	-	-	27	99.1	83	86

* Expressed in $mg \cdot L^{-1}$.

Mixed liquor solids data in Table 8 indicate that the volatile fraction increased from 37 to 70% when the feed was pretreated for calcium removal. Phosphorus requirements for system C were reduced markedly; rough balances indicated a tenfold reduction in P requirement. This observation tended to indicate the inorganic material precipitating in system A, was a calcium phosphate. To confirm this, and to define the structure of the precipitate, sludge samples were analyzed by x-ray diffraction (XRD) and scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS) analysis. XRD analysis indicated the inorganic phase in sludge A to be calcium phosphate tetrabasic ($4\ CaO \cdot P_2O_5$) However, EDS. analysis would tend to indicate that the material is octa calcium phosphate.

In general, observation of sludge A showed that the calcium phosphate did not coat the floc. Rather, it was discretely precipitated throughout the floc suspension and could not be responsible for any reduction in performance. This data complements the process data which showed no difference in performance between systems A and C.

Part 5 - Effect of Hydraulic Retention Time

In Phase I, studies were conducted at fixed anoxic and aerobic HRT's of one and three days, respectively. These values were chosen based on both theoretical and practical considerations, and included a safety factor of two. Since the HRT impacts severely on system capital costs, studies were conducted to define the limiting hydraulic requirements capable of effecting consistent nitrification. This was accomplished by operating the three systems in parallel at varying HRT's; 0.5, 0.67, and 1.0 day for the anoxic reactors and 1.1, 2 and 3 days for the aerobic reactors. The experimental conditions evaluated, and steady state reactor conditions achieved, are shown in Table 10. Mean effluent quality achieved at these operating conditions is summarized in Table 11.

A general deterioration in effluent quality with decreasing aerobic HRT was observed with increasing effluent SS, FOC and phenol and an increasingly unstable nitrification process as shown in Figure 4. These effects may have been compounded by the decreasing adsorptive capacity of the decreasing PAC loading at the lower HRT's. An increase in the level of effluent organic nitrogen with decreasing HRT may have been due to the presence of heterocyclic nitrogenous compounds that were not adsorbed by the PAC and which may, therefore, have contributed to the inhibition of nitrification.

Table 10, STEADY STATE OPERATING CONDITIONS - HRT EFFECT

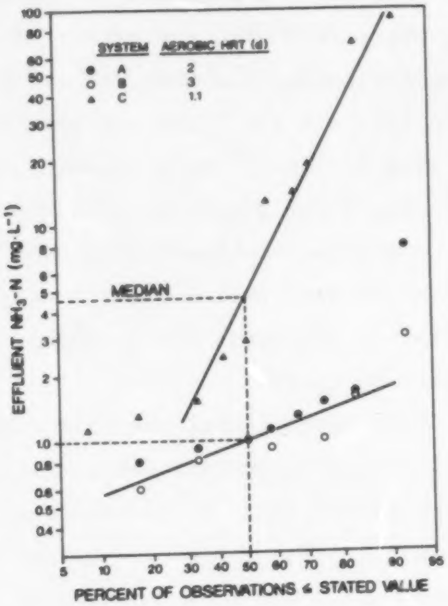
Reactor	HRT (d)		SRT (d)		Average Reactor Solids ($mg \cdot L^{-1}$)			Equivalent PAC Feed	Clarifier Effluent VSS
System	Anoxic	Aerobic	Anoxic	Aerobic	Biological MLVSS	MLSS	PAC	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)
A	0.67	2	10	30	5 500	16 200	500	33	18
B	1	3	10	30	3 630	9 550	500	50	10
C	0.5	1.1	15	30	6 920	13 840	500	18	49

Table 11, MEAN REACTOR EFFLUENT QUALITY - HRT EFFECT

Reactor		Anoxic Reactor		Aerobic Reactor									
System		FOC	NO_T-N	FOC	Phenol	TKN	NH_3-N	NO_2-N	NO_3-N	TCN	CNS	ON	TN
A	Effluent*	119	0.5	41	0.084	7	1.7	3.0	18.7	8	1.1	2.2	28.7
	% Removal	-	-	94.5	99.8	96.0	98.0	-	-	21	99.5	91	84.4
B	Effluent	114	0.7	38	0.072	7	1.1	9.7	8.3	8.1	1.1	1.2	25.0
	% Removal	-	-	95.0	99.8	96.0	98.7	-	-	21	99.5	95	86.0
C	Effluent	106	0.8	60	0.098	27	19.8	8.3	3.4	8.3	1.4	4.1	38.7
	% Removal	-	-	91.9	99.7	86.5	78.7	-	-	18	99.4	84	80.0

* Expressed in $mg \cdot L^{-1}$.

Denitrification did not appear to have been affected by HRT over the range examined (Figure 5) indicating that the full denitrification capacity of the system had not been exploited.



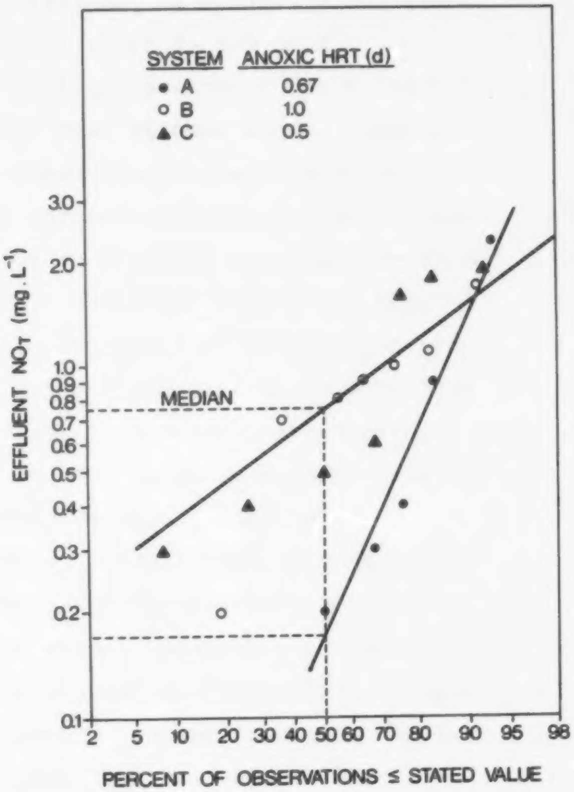


Figure 4, Effluent NH_3-N Data; HRT effect.

Figure 5, Denitrification performance; HRT effect.

TRACE ORGANICS REMOVAL

Coke production generates a great variety of poly-nuclear aromatics (PNA's) many of which are not identified in the list of priority pollutants. The U.S. EPA have shown[7,13] that adsorption was the main removal mechanism for PNA's in sewage treatment plants. The analysis of trace organics in this study was conducted to identify and quantify these compounds.

Aliquots of feed, final effluent and waste activated sludge from systems A and C were analyzed by GC/MS and HPLC for the presence of trace organics. These samples were taken during the period when the effect of calcium on nitrification performance was being evaluated, and thus the reactor conditions and effluent quality depicted in Tables 8 and 9 are representative. Both systems were operated at 40-day SRT, with 500 $mg \cdot L^{-1}$ PAC. However, the aerobic HRT's were different - 3 days in system A and 2 days in system C. Some selected data is shown in Table 12. It must be mentioned that only one replicate of each sample was analyzed, and while the limited quality assurance program indicated good recoveries of spiked compounds (58 to 108%), the absolute values reported must be treated with caution.

The data indicated the presence of 16 base-neutral and acid extractable priority pollutants. In addition, 32 non-priority pollutants, primarily heterocyclic nitrogenous compounds, were identified. These compounds could not be quantified due to lack of standards. The units expressing trace organic concentrations have been selected to facilitate data comparisons on a similar numerical basis. Concentrations are expressed at a ppb level in both the liquid streams and the sludge so that the fate of the trace organics may be traced more easily through the treatment process. Operation at a 3-day aerobic HRT generally produced a 'cleaner' effluent, with marked improvement in removal of PNA's. Not all PNA's were accumulated in the sludge. Of the PNA's in the feed only indeno-pyrene, naphthalene, pyrene and benzo-a-anthracene were adsorbed on the sludge. Although significant quantities of phthalates and naphthalene accumulated in the sludge, mass balances indicate that more than 90% of those compounds were biologically degraded. In contrast, the indeno-pyrene and pyrene remained adsorbed on the sludge.

A substantial concentration of organics can occur which illustrates the role of the sludge as a "sink" for some organics. Benzo-a-anthracene, for example, was not detected in the feed but was present at 360 ng/g in the sludge. Mass balance calculations show that, assuming no losses to other removal mechanisms, a concentration factor of approximately 4000 was in effect.

Table 12, SELECTED TRACE ORGANICS DATA

	System 'A'			System 'C'			Detection Limit ($\mu g \cdot L^{-1}$)
	Feed ($\mu g \cdot L^{-1}$)	Effluent ($\mu g \cdot L^{-1}$)	Sludge ($ng \cdot g^{-1}$)	Feed ($\mu g \cdot L^{-1}$)	Effluent ($\mu g \cdot L^{-1}$)	Sludge ($ng \cdot g^{-1}$)	
Anthracene	1.0	0.3	ND	1.0	1.4	ND	0.25
Benzo-a-pyrene	0.5	0.4	ND	ND	1.5	ND	0.1
Chrysene	4.0	1.7	ND	18	4.0	ND	0.4
Diethylphthalate	300	100	9 100	1 310	110	6 600	10.0
Bis (2 ethyl hexyl) phthalate	Trace	Trace	11 000	150	Trace	20 000	10.0
Fluoranthene	2.6	1.0	ND	4.1	2.0	ND	0.1
Fluorene	4.0	1.5	ND	3.0	3.0	ND	1.0
Indeno pyrene	0.7	0.2	9 500	1.2	ND	1 800	0.2
Naphthalene	760	ND	7 900	3 800	ND	2 600	10.0
Phenanthrene	3.5	0.75	ND	Trace	0.5	ND	0.4
Pyrene	2.2	0.7	740	ND	2.0	ND	0.6
Benzo-a-anthracene	ND	ND	360	ND	ND	160	0.6
Cl Pyridine	++	ND	+	++	ND	+	
Quinoline	++	ND	+	++	ND	+	
1H Indole	++	ND	+	++	ND	+	
9H Carbazole	++	ND	++	++	ND	++	
9H Anthracene Carbonitrile	+	ND	++	+	ND	++	
Phenanthridine	+	ND	ND	+	ND	++	
Phenanthridinone	+	ND	+	+	ND	++	
Indolizine	+	ND	ND	+	ND	++	

Note: Sludge values reported on a dry sludge basis.
ND = not detected.
+ = a minor peak.
++ = a major peak.

The feed concentration of benzo-a-anthracene would then have been 0.09 $\mu g \cdot L^{-1}$ which is below the detection limit of 0.6 $\mu g \cdot L^{-1}$. It could be concluded that other organics are undetected in the feed but will be adsorbed to significant levels in the sludge.

None of the heterocyclic nitrogenous compounds identified in the feed could be detected in effluents A or C . However, compounds such as 9H carbazole, 9H anthracene carbonitrile, indolizine, phenanthridine and phenanthridinone were accumulated in the sludge.

The degree to which PAC addition aided in adsorption of PNA's and heterocyclic nitrogenous compounds could not be determined. The literature[14]. does, however, indicate that many PNA's are readily adsorbed by PAC. No conclusive evidence has been generated to identify the mechanism by which PAC addition prevents inhibition of nitrification but it is possible that this occurs by the adsorption of the heterocyclic nitrogenous compounds.

CONCLUSIONS

1. Complete nitrogen control of Dofasco coke plant wastewater can be achieved in a single sludge pre-denitrification nitrification system only by the addition of low levels of PAC (at approximately 50 $mg \cdot L^{-1}$).
2. Over the temperature range, 20-24°C, nitrification was stable at aerobic HRT's in excess of two days; denitrification is stable at anoxic HRT's of 0.5 day or greater.
3. The organic carbon in the wastewater can be utilized as the energy source during denitrification. At FOC/TKN ratios ≥ 3.5, carbon supplementation is not required.
4. The presence of high levels of calcium in the wastewater does not affect nitrification.
5. The efficient operation of the ammonia still is critical to the maintenance of a stable nitrification process. It is essential to minimize variation in wastewater ammonia levels: TKN_{max}/TKN_{mean} should be should be ≤ 2.0.
6. GC/MS analysis identified 32 heterocyclic nitrogenous compounds and 16 priority pollutant organics in the feed. The pre-denitrification nitrification system, with PAC addition, operated at a high SRT and HRT, is capable of effecting good removal for most of these organics. Both adsorption and biodegradation are major removal mechanisms.

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AN INVESTIGATION OF FOREIGN BY-PRODUCT COKE PLANT AND BLAST FURNACE WASTEWATER CONTROL TECHNOLOGY

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ABSTRACT

A study was made to determine if more advanced processes for the treatment of by-product coke plant and blast furnace gas cleaning wastewaters were used in foreign plants than in domestic ones. Some unusual techniques for the treatment of blast furnace gas cleaning wastewaters were found. Aeration of gas cleaning wastewater prior to clarification improved settling and resulted in a greater rate of recirculation. Filtering the wastewater through slag or flue dust removed cyanide although the removal mechanisms is not known.

Treatment of by-product coke plant and blast furnace gas cleaning wastewater is, generally, not more advanced in foreign plants than in the United States. However, blast furnace gas cleaning water in foreign plants is generally recycled to a greater degree.

Discussions were held with plant and corporate personnel at 26 plants in 14 countries and with regulatory agencies in 10 of the 14 countries, to determine the regulations imposed upon the plants, the incentives provided to reduce pollution loads to receiving waters and to investigate treatment technology.

Recommendations for research projects are made as there appears to be promising areas for improvement of wastewater treatment techniques.

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INTRODUCTION

In its continuing effort to make information available on the most advanced and efficient methods of reducing water pollution from iron and steel production, the U.S. EPA Industrial Environmental Research Laboratory, Research Triangle Park, NC, contracted with Hydrotechnic Corporation to perform an engeneering study of foreign steel plants. This was to determine if there were water pollution control practices being employed for by-product coke plant and blast furnace wastewaters that were superior to those used in the United States. In fulfillment of this contract Hydrotechnic visited 25 plants in 14 countries. Plants in the United States, Canada and Eastern Bloc nations were not included. The plants visited account for over 23 percent of the steel produced outside of the three areas mentioned. One of the plants visited was a by-product coke plant only and one plant consisted of a single blast furnace. Neither of these plants had other production facilities normally associated with steel plants.

Three factors were considered in determining the selection of the plants to be evaluated:

- Based on published literature and personal correspondence, the likelihood of the plants utilizing exemplary or innovative treatment technology.

- Based on prior investigation, the relative abundance or lack of water in the plant area.

- Based on published information, the degree of environmental concern in the countries where the plants are located.

Of the 25 plants visited, 23 provided information that was useable to permit evaluation of their wastewater treatment systems. These 23 plants are listed below by country.

ARGENTINA - Plant requested anonymity
AUSTRALIA - Broken Hill Proprietary - Newcastle Works
- Australia Iron & Steel - Hoskins Kembla Works
BELGIUM - SIDMAR
ENGLAND - British Steel - Scunthorpe Works
- Orgreave Works
FRANCE - Pont-a-Mousson
ITALY - Italsider - Taranto Works
JAPAN - Nippon Kokan KK - Ogishima Works
- Sumitomo Metal Ind. - Kashima Works
- Kobe Steel Ltd. - Kakogawa Works
- Kawasaki Steel - Chiba Works
MEXICO - Altos Hornos de Mexico
NETHERLANDS - Hoogovens
SOUTH AFRICA - ISCOR - Pretoria Works
- Newcastle Works
- Vanderbijlpark Works
SWEDEN - Svenskt Stal - Norrbottens Jarnverk
- Surhammars Bruks - Spannarhyttan
TAIWAN - China Steel
WEST GERMANY - Roechling Burbach
- Thyssen
- Hoesch Huttenwerke

In addition to visiting plants and corporate engineering staffs, and observing wastewater treatment operations at the production facilities, nine government agencies were consulted. In a tenth country a trade association was consulted. The agencies provided information on how regulations affected the degrees of treatment and on the incentives provided for increasing recirculation of water within the production facilities.

The nine governments were:

- Argentina
- Australia (New South Wales)
- Japan (two agencies)
- Mexico
- Netherlands (two agencies)
- South Africa
- Sweden
- Taiwan

At the meeting with the trade association,VDEh representing the West German Iron and Steel Industry, a representative from the local West German water and waste agency was present.

SUMMARY

1. By-Product Coke Plants

The volume of waste ammonia liquor produced at foreign by-product coke plants ranged from 0.14 to 0.24 m^3/Mg (34 to 178 gpt).

These volumes are higher than those encountered in the United States by-product coke plants evaluated.

The treatment of by-product coke plant wastes at foreign plants is basically similar to that practiced in the United States. Single stage biological treatment is used at 14 of the by-product coke plants visited. Nine of these fourteen plants add dilution water to reduce high ammonia concentrations in the wastewater to levels not toxic to the organisms. At one plant in Japan salt water is used. All plants utilizing biological treatment add nutrients, usually in the form of phosphoric acid. Two of the plants pretreat the wastes by filtering the wastewater through a coarse coke bed. This procedure removes tar that may be detrimental to the biological oxidation process. Two other plants further treat their effluent by sand filtration and, following, by activated carbon adsorption.

Of the 23 by-product coke plants for which some data was available, fourteen plants discharged their biologically treated wastewater to public waters, five plants treated their wastewater in free ammonia stills and then discharged them, one plant treated its wastewater in both free and fixed ammonia stills prior to discharge, one plant utilized a free ammonia still and a dephenolizer prior to discharge, one plant provides no treatment at all prior to discharge and one plant uses the raw waste ammonia liquor to irrigate a grass crop that is used for animal feed, reportedly with no ill effects to the animals.

2. Blast Furnaces

Blast furnace gas cleaning systems were used at all of the plants visited. The gas washer wastewater application rate varied depending on the wet type of gas cleaning system used. The rates varied from 2.1 to 28 m^3/Mg (507 to 6715 gpt) of iron produced. The weighted average application rate was 6.09 m^3/Mg (1460 gpt).

All but one of the plants visited treat their gas washer wastewater for solids removal prior to reuse or discharge. This plant is under Government directive to provide treatment within the next two years. Of the 23 blast furnace installations studied, three do not recycle their wastewaters. The remaining 20 plants have recycle rates ranging from 27.4 to 99.2 percent with a weighted average rate of 92.4 percent.

Two of the plants provide treatment of their blowdowns for cyanide removal. One uses alkaline chlorination and one uses Caro's Acid (H_2SO_5). Three other plants reported unexpected cyanide reductions which are not due to planned treatment. One of these plants reported that the cyanide reduction is a result of seepage of water through the accumulated sludge in its flue dust ponds; one reported cyanide reduction due to sparging of steam in its clarifier to prevent freezing, and the third reported cyanide reduction when the gas washer wastewater blowdown was used to quench slag.

3. Regulatory Agencies

Regulatory agencies of nine foreign governments were visited to gain insights into the regulatory climate and the relationship that these agencies have with industry. This information provides a better understanding of the individual plant pollution control practices. Countries that are members of the European Economic Community (EEC) have been issued a policy directive with regard to control of water pollution in the community. To date the regulations of the individual countries have taken precedence over the EEC directive.

In addition to the regulatory agencies, VDEh, a West German trade association which represents the iron and steel industry, was visited. In attendance at the meeting with VDEh were representatives from several steel corporations and a representative of a local West German Federal Government authority.

Only two of the ten countries from which regulations were obtained have or will have regulations specific to the iron and steel industry. All others have regulations which pertain to the quality of water discharged to, or the effect of the discharge on, the receiving body. The regulations are based upon the use that is made of the receiving body: i.e., potable water, fishing, recreation, etc.

It was reported that input from outside of industry had little effect in the establishment of regulations. Generally, the bases for regulations are: preservation of public health, minimizing environmental effects, aesthetic considerations and water conservation. The economic impact of the regulations on the individual plant, the industry and the country is considered.

All agencies reported that the industries or individual companies to be affected by proposed regulations are conferred with prior to the establishment of the regulations.

In all of the countries variances to the regulations are subject to negotiation both prior to and subsequent to promulgation. They may be based upon available technology and/or economic conditions. The final regulations as they apply to the individual plants may be referred to differently in each countries, e.g., in England, they are called "consent conditions" and in South Africa, "relaxed standards."

4. Comparison between Foreign and United States Treatment

A comparison of foreign and United States by-product coke plants and blast furnace wastewater treatment systems reveals that:

- in general, the treatment applied to these wastewaters in foreign plants is similar to that used in United States plants;

- effluents from foreign plants are not monitored for pollutant content to the same degree that United States plants are, i.e., more parameters are monitored in the United States than in foreign countries;
- foreign plants generally recirculate blast furnace gas washer water to greater degrees than do United States plants.

Table 1 shows the comparative compliance with United States effluent guidelines limitations as presented in the "Draft Development Document for Proposed Effluent Limitations and Standards for the Iron and Steel Manufacturing Point Source Category" (EPA 400/1-79/024a, October 1979) for the foreign plants observed and the plants for which detailed data was available in the United States.

An indication of water use efficiency can be obtained by comparing the degrees of EPA compliance to mass limitations. A larger portion of the foreign blast furnace treatment systems that meet the guidelines limitations at BAT levels with respect to concentrations also meet the guidelines limitations with respect to mass discharges for suspended solids and cyanide. This indicates that less water is being discharged per unit of production resulting in the lower mass discharges.

TABLE 1. COMPARATIVE COMPLIANCE OF FOREIGN AND U.S. BY-PRODUCT COKE PLANT AND BLAST FURNACE WASTEWATER TREATMENT FACILITIES WITH U.S. EPA DRAFT EFFLUENT GUIDELINES FOR BPT AND BAT

AREA	COKE PLANT OR BLAST FURNACE	LEVEL OF TREATMENT	PARAMETER (EXCLUDING PRIORITY POLLUTANTS)								
			SUSPENDED SOLIDS	CN	CNS	OIL AND GREASE	PHENOL	PHENOLICS	AMMONIA	SULFIDE	FLUORIDE
FOREIGN	BY PRODUCT COKE PLANT	BPT	5 100% 100%	10 100% 100%	NL	2 100% 100%	11 73% 45%	NR — —	9 11% 22%	NL	NL
U.S.	"	"	5 60% 60%	5 100% 80%	NL	4 50% 75%	4 100% 100%	5 67% 67%	5 40% 60%	'NL	NL
FOREIGN	"	BAT	5 80% 80%	10 70% 50%	2 0% 0%	2 100% 100%	10 10% 10%	NR — —	9 11% 11%	1 0% 0%	NL
U.S.	"	"	5 40% 60%	5 0% 0%	5 0% 0%	4 50% 75%	4 50% 50%	2 50% 50%	5 40% 40%	4 25% 50%	NL
FOREIGN	BLAST FURNACE	BPT	13 100% 69%	14 100% 93%	NL	NL	2 100% 100%	NL	5 100% 60%	NR — —	5 40% 80%
U.S.	"	"	6 100% 100%	6 83% 67%	NL	NL	6 100% 83%	NL	6 100% 83%	6 83% 67%	5 100% 80%
FOREIGN	"	BAT	13 8% 15%	14 29% 29%	NL	NL	2 50% 50%	NL	5 20% 0%	NR — —	5 20% 0%
U.S.	"	"	6 17% 0%	6 33% 17%	NL	NL	6 50% 33%	NL	6 33% 0%	6 40% 0%	5 40% 0%

No. OF PLANTS FOR WHICH DATA IS AVAILABLE	
% THAT MEET CONCENTRATION LIMIT	% THAT MEET MASS LIMIT

NL	NO U.S. LIMITATION
NR	NO DATA

NOTE: The data presented in this table are based on information from a limited number of plants.

The U.S. plants are only those for which data were available from the U.S. EPA Draft Development Documents.

The data for foreign plants are for those that were visited during the course of the study and constituted plants thought to have superior technology.

5. Other Observations

While visiting Australia the opportunity to visit the John Lysaght (Aust.) Ltd. organization was taken to discuss the hot and cold mill water systems at its Westernport Bay facility. The hot strip mill operates with the lowest blowdown of any such facility in the world and features four recirculating water systems. One is a completely closed non-contact cooling water systems for the reheat furnace skid cooling. The other three systems have the water cascaded with the makeup water consisting of a mixture of a purchased supply and collected storm water. The makeup is applied to the area where highest quality water is required. Blowdown is cascaded from high water quality systems to facilities which may tolerate lower quality. The contact cooling water is filtered, cooled and recirculated. Blowdown from the system discharges to Westernport Bay via the plant's cold mill effluent lagoon. The plant reports that the total discharge from the mill is 0.2 m^3/Mg (48 gpt) with mass discharges of 0.002 kg/Mg (lb/1000lb) each of suspended solids and oil.

Their cold mill complex consisting of a hydrochloric acid pickler, a five stand cold reduction mill, a coating line and a paint line is also an excellent example of conservation and reuse which also results in significant pollution control. The key to minimizing plant water use is the segregation of water systems. All non-contact cooling water is collected, cooled and reused in a separate system. Sanitary sewage is collected and treated separately. Waste pickle liquor is regenerated in a hydrochloric acid regeneration plant.

The process water is treated in two separate systems: one is the industrial water treatment system in which the relatively clean wastewater from stands 1 and 5 of the cold mill and the picler process water are treated, cooled, combined with tertiary treated sanitary wastes and returned to the mill for reuse. The second wastewater treatment system receives the cold mill rolling solution blowdown and dumps, the pickle liquor regeneration plant excess rinse water, galvanizer alkali dumps, and the industrial water treatment plant blowdown. These wastes are treated for discharge to receiving waters.

INNOVATIVE TECHNOLOGY

1. Blast Furnaces

A unit operation, not known to be practiced in the United States, was observed at two foreign plants, August Thyssen in West Germany and Chiba Works of the Kawasaki Steel Corporation. It is the aeration of gas washer water prior to settling in clarifiers or thickeners. A portion of the settled sludge is recirculated back to the aeration basin to act as a seed for precipitation of carbonates. The purpose of this operation is to increase the cycles of concentration while not increasing the likelihood of scale formation in the recirculation system.

Four methods of cyanide removal other than alkaline chlorination from gas washer wastewater were noted. Three of these methods were not utilized as intentional unit operation, i.e.,the purpose of the operation was not for the specific purpose of cyanide removal although removal was noted. These operations are:

- Sparging steam through the waste. At one plant in Sweden (Spannarhyttan) cyanide reduction was noted after steam sparging. Steam was utilized to prevent freezing of water in the clarifier and apparently resulted in cyanide reduction from an influent concentration of 30 mg/l to 2.4 mg/l.

- Filtration of blast furnace wastewater through flue dust. Two plants owned by Hoesch Estel in West Germany utilize sludge disposal as the means of blast furnace gas washer water blowdown. The sludge is discharged to flue dust ponds and the excess water seeps through, is collected in an underdrain pipe, and discharges to a river. Alkalinity is added at both plants, at one in the form of cold mill sludge and at the other in the form of caustic (sodium hydroxide). It was noted that the cyanide concentration in the liquid phase of the sludge was 0.2 mg/l and the cyanide concentration of the underdrain flow was 0.1 mg/l. The plant has theorized that the reduction is due to metallo-cyanide complexes being formed and being adsorbed on the flue dust. No work has been done to confirm this hypothesis.

- Use of gas washer wastewater for slag quenching. One plant, ISCOR's Pretoria Works in South Africa, reported that when a portion of the gas washer wastewater blowdown is used for slag quenching the leachata from the slag pile is free of cyanide. The plant has not reported the cyanide content of the raw water but stated that they believe that the reason for the lack of cyanide in the leachata is due to biological activity in the slag pile. No work has been done to verify this hypothesis.

- Pont-a-Mousson in France uses Caro's Acid (H_2SO_5) for cyanide destruction. The plant discharges a quantity of gas washer water from the flue dust settling pond on a batch basis to chemical treatment tanks where Caro's Acid is added. It reacts with and oxidizes the cyanide. In the process some phenol reduction is also observed.

2. Coke Plants

Of the 23 by-product coke plants observed, 14 utilize biological methods for treatment of their wastewater. At China

Steel the by-product coke plant wastes are pretreated by filtration through a bed of coke to remove excess tars that might interfere with the biological process. After the filtration step, sanitary wastes from the entire plant are combined with the coke plant wastes and treated in an activated sludge process.

One plant combines untreated coke plant wastewater with blast furnace gas washer water blowdown and uses the combined wastes for irrigation of grass fields. The grass crop is used for cattle fodder. No ill effects to the cattle have been reported. This method cannot be considered as innovative treatment but rather as an innovative means of disposal.

OTHER OBSERVATIONS

Plant and corporate managements are intimately familiar with wastewater treatment practiced at the individual plants and are usually apprised of potential problems before they actually occur. Operators, in many cases, are familiar with the theoretical as well as the practical aspects of the treatment plant operations.

Generally, housekeeping was observed to be of a high order. Water was not running where it was not needed. In plants where space permitted green areas were set aside both to enhance the appearance of the physical plant and to reduce noise in the plant environs.

In one blast furnace cast house all runners were covered with hoods and a vaccum applied. This resulted in a noticeable lack of fugitive emissions.

CONCLUSIONS

Based on observation at 25 foreign plants visited that operate either by-product coke plants or blast furnaces, or both, it is concluded that the wastewater treatment practiced in forign plants is basically similar to that practiced in the United States. Generally, blast furnace gas washer water is recirculated to a greater degree than at United States plants.

Two plants in Japan reported that the by-product coke plant wastewater passed through a tertiary treatment phase, i.e., sand filtration followed by activated carbon adsorption. Of all the plants observed or reported, these were the only plants that apparently addressed the problem of priority pollutants; however, no data with regard to the efficiency of removal of priority pollutants or effluent levels was provided when it was requested.

Foreign effluent quality regulations are usually negotiated between government and industry on a case by case basis. The economic impacts of the regulations are a major concern.

RECOMMENDATIONS

Research should be conducted to quantify the pollutant reductions attainable and to ascertain the mechanisms by which the reduction of cyanide occurred for two of the methods observed. These methods are:

- Sparging of steam through wastewater. Research on this method should also include the effects on air quality and energy requirements.

- Filtering the wastewater through flue dust. The research on this method should also include the possible effects on the air quality at sinter plants or briquetting plants if the cyanide containing flue dust is used as a feed stock.

Research should also be conducted to determine the effect of increased recirculation at blast furnace gas washer operations. Specifically, the method of increasing recirculation by aerating the solids laden gas washer water prior to settling should be investigated.

Treatment of by-product coke plant wastes by biological means is a generally accepted and proven procedure. However, the authors believe that coke plant wastewater can be combined with blast furnace gas cleaning blowdown water prior to treatment. During discussions with steel plant personnel both in the

United States and abroad, this concept was raised. The only concrete objection raised was that the heavy metals present in the blast furnace wastewater would be toxic to the biological systems. However, fluoride which is present to some degree in blast furnace gas washer wastewater, is a limited U.S. guideline parameter and lime precipitation will be required to remove the fluoride. When lime is added to precipitate calcium fluoride, hydroxyl ions will, at the proper pH values, form metal hydroxide precipitates. The removal of these precipitates should reduce heavy metals to varying degrees to levels that would be well below those toxic to biological systems. Therefore, when lime is added, two benefits are realized: (1) the fluorides are reduced to acceptable levels, and (2) toxic metals are reduced to permit discharge to a biological system where the regulated biodegradable contaminants can be oxidized. Confirmation of this concept should be proven by a research program.

Further research should be performed to verify a second stage biological process to nitrify the ammonia in the combined wastewater streams.

SETEC-CE-80-044

FACTORS INFLUENCING BIOLOGICAL NITRIFICATION OF STEEL INDUSTRY WASTEWATERS

by

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ABSTRACT

Laboratory experiments were conducted on the rate of ammonia bio-oxidation by an autotrophic culture of strict nitrifiers. The quantitative influence of pH, un-ionized (free) ammonia, phenol and elevated temperatures on Michaelis-Menten type nitrification biokinetics was evaluated.

Total ammonia and pH act via a "substrate inhibition" mechanism to nitrification. The maximum specific rate of nitrification decreases proportionally to the square root of ambient phenol concentrations. Temperatures in excess of 30°C decrease the maximum specific rate of nitrification, decrease nitrifier yield coefficients, nad increase the "Michaelis-Menten" constant leading to an overall decrease in rate kinetics and potential process instabilities at such elevated temperatures. Conclusions based on engineering calculations are presented to illustrate design and operational considerations for the biological removal of wastewater ammonia.

KEYWORDS:

nitrification; biological treatment; activated sludge; biokinetics; phenol; nitrosomonas; free ammonia; toxic inhibition; temperature; coke plant; steel industry;

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"FACTORS INFLUENCING BIOLOGICAL NITRIFICATION OF STEEL INDUSTRY WASTEWATERS"

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INTRODUCTION

The overall objective of this research is to conduct basic studies into possible causes of biological nitrification process instability as currently observed in many industrial wastewater operations, and in the longer term, to propose rational and pragmatic process operational alternatives for the biological oxidation of ammonia.

Research activities to date have centered on quantification of the influence of key reproducible parameters on the biokinetics of nitrification, and calculations to illustrate the effect of changed biokinetics on nitrification process design and operational strategies (1,2).

Theoretical Considerations

Although several genera of autotrophic bacteria have been identified as capable of causing nitrification, the genera nitrosomonas and nitrobacter are considered responsible for most naturally occurring nitrification as:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{nitrosomonas}} 2\,NO_2^- + 4H^+ + 2H_2O \qquad (1)$$

and

$$2NO_2^- + O_2 \xrightarrow{\text{nitrobacter}} 2NO_3^- \qquad (2)$$

The key to a rational utilization of any biological process to non-stereotyped applications is an understanding of the appropriate biokinetics and defining bio-relationships. For nitrification applications, it has been found that appropriate utilization of Michaelis-Menten kinetic theories can serve in most cases to describe the system with reasonable clarity. Accordingly, the specific experimental goal of this research effort is to develop, from a deterministic base, modifications of nitrification bio-kinetic relationships described by Michaelis-Mentel kinetics to account for apparent industrial process instability observations.

Nitrification process instability can be caused by the interactions of organic "external agent" via a toxic inhibition mechanism, and/or via a substrate inhibition mechanism with high enough levels of un-ionized ammonia as governed by the aqueous ammonium-ammonia equilibria.

In addition, all biological organisms exhibit optimum temperature ranges for substrate utilization. At lower temperatures, classical Arrhenius theory predicts a decrease in reaction rates, while at elevated temperature, simultaneous enzyme-protein denatuation predicts a similar decrease in rate biokinetics.

Biokinetics

The defining equations for biological reactions may be written by equations 3 and 4 as:

$$v = V_{max} S / (K_m + S) \qquad (3)$$

where;

v = specific nitrification rate (lb NH_3 used/lb VSS-day)

V_{max} = maximum specific utilization rate

K_m = "Michaelis-Menten" constant (mg NH_3/L)

S = substrate level (mg NH_3/L)

and

$$dX/dt = a(dS/dt) - bX \qquad (4)$$

where;

X = biomass concentration (mg VSS/L)

t = time

a = yield coefficient (lb VSS grown/lb NH_3 utilized)

b = decay coefficient (1/time)

The above equation is often approximated by a one-constant equation of the form:

$$\Delta X = (a)_{ob} \Delta S \qquad (5)$$

for conditions of steady state continuous culture performance. The observed net yield coefficient, $(a)_{ob}$, is the measured harvest of biomass per unit ammonia removed.

Substrate Inhibition Models

Many substances act as nutrients at low concentration levels, and serve to inhibit biokinetics at higher levels.

Mathematically, the relationship for substrate inhibition may be modified from equation (1) as :

$$v = Vmax / \{ 1 + (Km/S) + (S/Ki)^n \} \qquad (6)$$

where Ki = inhibition constant

n = order of inhibition

This type of relationship has been found to best describe nitrification biokinetics as will be shown below.

EXPERIMENTAL APPROACH

A culture of nitrifying organisms was developed in our laboratory two years prior to undertaking this effort. The organisms were acclimated to a synthetic ammonia waste, with sufficient inorganic carbon (sodium bicarbonate) and trace nutrients in open semi-continuous systems with hydraulic detention times of about 2 days and sludge ages varied in the range of 5 to 20 days. At no time during the course of this research were the organisms fed any carbon source nutrient other than inorganic carbon. The organisms exhibited a red color found to be typical of pure nitrification bio-systems.

The experimental approach to determining biokinetics under a variety of conditions is that of batch respirometric evaluations. The philosophy behind this approach is to measure specific oxygen utilization in a constant temperature chamber fitted with a dissolved oxygen probe so that the initial sample would not be destroyed upon monitoring and analysis. It was noted consistently during the course of these experiments, that ammonia was oxidized to nitrite, and at no time during testing was nitrite oxidized to nitrate. Thus for purposes of this research, oxygen utilization data could be directly correlated with specific rates of ammonia oxidation in direct respirometric evaluations.

A calibrated Orion specific ion probe with Orion model 407 analyzer was used for all ammonia analysis. Alkalinity, volatile suspended solids, nitrite, nitrate, and other trace material analysis were conducted in accord with Standard Methods (3).

Un-Ionized Ammonia Kinetic Considerations

Aqueous ammonia is thought to undergo the following reactions in water:

$$H_2O + NH_3 = NH_4OH_{total} = NH_4^+ + OH^- \qquad (7)$$

$$\text{where } H^+ + OH^- = H_2O$$

The total ammonia in an aqueous solution is the sum of the un-ionized and ionized forms of ammonia, for which all practical purposes is

$$NH_{3\ total} = \underbrace{NH_3 + NH_4^+}_{\text{un-ionized and ionized}} \qquad (8)$$

From the equilibrium expression for the dissociation of un-ionized ammonia

$$K_1 = \frac{(NH_4^+)\ (OH^-)}{(NH_{3aq})} \qquad (9)$$

and

$$K_w = (H^+)\ (OH^-) \qquad (10)$$

the following may be derived for the ratio of un-ionized ammonia to total aqueous ammonia as:

$$R = \frac{NH_3 \text{ un-ionized}}{NH_3 \text{ total}} = \frac{1}{1 + \frac{(K_1)}{K_w}(H^+)} \qquad (11)$$

Thus, the ratio of un-ionized ammonia to total ammonia in a stream is a function of pH and temperature, with temperature influencing the numerical values of K_1 and K_w.

Figure 1 is a summary plot of specific ammonia utilization rate ($v = gNH_3$ used/gvss-Day) as a function of aqueous un-ionized ammonia level at pH=8.0.

The equation of the smooth curve fit through data points is:

$$v = 1.2 \; / \; \left(1 + \frac{0.184}{NH_3} + \frac{NH_3}{500}\right) \qquad (12)$$

It should be noted that in these equations, the order of inhibition (n) is one.

Table 1 is a summary of results of correlation of all laboratory data in accord with the substrate inhibition equation #6.

TABLE 1

Summary of Nitrification Biokinetic Parameters

PH	V_{max} g NH_3/g VSS-DAY	K_m mg/L NH_3	k_i mg/L	n
7.0	0.7	0.184	500	1
8.0	1.2	0.184	500	1
9.0	0.95	0.184	200	1

Application to Design and Operation

Using values of yield coefficient "a" of 0.13 g VSS/g NH_3 and decay coefficient "b" of 0.04 DAY as also found in this research, an overall equation relating sludge age (θ) to effluent ammonia from a one stage activated sludge reactor may be derived as:

$$\frac{1}{\theta} = a\,(v) - b \qquad (13)$$

Figure 2 is a series of calculated curves predicting the influence of pH and sludge age on effluent total ammonia (ionized + un-ionized). This curve was calculated from laboratory data presented on Table 1 and figure 2 coupled with the ammonia-ammonium/pH equilibrium relationship of equation 9. Also outlined on this figure is a proposed Pennsylvania discharge standard of 10 mg NH_3/L illustrating the influence of pH and sludge age to meeting this standard.

INFLUENCE OF ELEVATED TEMPERATURES ON NITRIFICATION

While much Municipal oriented research has been conducted on the effect of low temperatures on nitrification, little research to date has been published on the influence of elevated temperatures on nitrification biokinetics.

There is some controversy in the literature as to the optimum temperature for nitrification. Buswell et al., (4) cite 30°C to 36°C as the optimum for *Nitrosomonas*. Painter and Loveless (5) reported 34°C to 35°C as an optimum for *Nitrobacter*, while Laudelot and VanTichelen (6) found 42°C was the best for the same organisms. Gibbs (7) reported that 53°C to 55°C inactivated nitrifiers. Sawyer and Bradney (8) in their BOD work showed that pasteurization at 55°C proved very effective in the inactivation of nitrifiers. Shammas, in his doctoral dissertation (9), indicated no optimum temperature for nitrification with a constant "activity" in the temperature range of 15°C to 35°C with 50 percent of the nitrification activity (rate) occurring at around 12°C.

It has been assumed by many that the cell synthesis coefficient remains constant and independent of temperature. Sayigh and Malina (10), Zononi (11), and Sawyer and Rohlich (12) however, have shown this assumption *not* to be true. Sayigh and Malina (10) observed cell synthesis coefficients of 1.67, 1.35, and 1.52 (lb MLVSS synthesized/lb soluble COD removed) at 4°C, 10°C, and 20°C respectively. At 31°C, they showed the cell synthesis coefficient decreasing to 0.62.

Experimental

For this series of experiments, the nitrifiers were *acclimated* to specific temperatures by equipping the complete mix semi-continuous reactors with inexpensive "fish tank heaters". The sludge was held at the desired temperature for a period of at least two sludge ages prior to data gathering. Data was collected in a manner similar to the the above except that a specially designed reactor with water bath was employed. The steady-state data presented below are for nitrifiers acclimated to the temperatures indicated at pH = 8.0 .

Figure 3 is a plot of maximum specific ammonia utilization as a function of temperature illustrating that at a temperature range of 22°C to 30°C, Vm = 1.26 lb NH_3/lb VSS-day, and for temperatures in the range of 30°C to 45°C,

$$Vm = 3.78 - 0.084\ (T) \qquad (14)$$

Figure 4 is a plot of Km with temperature illustrating an apparent slope reversal at temperatures on either side of 30°C. Figure 4, is a plot of observed yield coefficient (defined in equation 3) as a function of temperature.

Application to Design and Operation

For any temperature, values of "Vm" and "Km" may be obtained. These values may be substituted into equation #3 for evaluation of "v" as a function of effluent ammonia (ammonia level surrounding the biota). This relationship may be substituted into equation 13 to develop a continuous relationship of sludge age (θ) vs. effluent ammonia at any given temperature. Figure 6 is a family of such curves of effluent ammonia vs sludge age as functions of wastewater temperature.

In order to best interpret the concepts developed by this figure, a cross plot of sludge age vs. temperature was developed for a family of effluent ammonia levels. This was done by placing horizontal lines across the curves of figure 6 at various effluent ammonia levels, and plotting the points of intersection on figure 7. The cross plots were done for effluent ammonia levels of 5 mg/L to 50 mg/L. As can be best seen from figure 7, the joint effects of temperature on Vm, Km, and yield coefficient as shown on figures 3,4,and 5 respectively serve to cause the nitrification process to become unstable at elevated temperatures. The relative flatness of the curve at temperatures below 30°C indicates a process stability for nitrification, which is also in accord with some steel industry observations.

From a biochemical viewpoint, the overall decrease in rate kinetics at temperatures observed in excess of 30°C may be anticipated due to progressive denaturation of enzyme proteins. Two simultaneous reactions are occurring at the same time; an increase in rate of biological nitrification (the foward reaction), coupled with an increased rate of chemical protein denaturation (an analogy to the reverse rate) resulting as an apparent optimum in overall reaction rate at a temperatureof about 30°C (86°F) followed by a decrease in overall nitrification rate as the temperature exceeds 30°C. It should be noted that extrapolation of kinetic parameter and yield coefficient data appears to show that an upper limit for sustained (but slow) biological nitrification for these mesophilic organisms is about 45°C (113°F); a value which closely agrees with textbook information on the microbiology of nitrosomonas organisms.

INFLUENCE OF TRACE ORGANICS-PHENOL

In summary of a third research effort in this overall project, phenol was found to effect only the Vmax term of equation #3 in a manner proportional to the square root of the phenol concentration(1). An overall rate expression for the influence of phenol on nitrification at pH=8.5 is:

$$v = \frac{4.14\ (N)}{\{4.4 + \sqrt{P}\}(2.78 + N)} \qquad (15)$$

An operational model of the form of equation #13 may be written as:

$$1/\theta = [0.13[\frac{0.92\ \{NH_3\text{-}N\}}{\{(1 + \frac{\sqrt{P}}{4.4})(2.78 + NH_3\text{-}N)\}}] - 0.04]\ \text{day}^{-1} \qquad (16)$$

SUMMARY OF RESULTS AND SPECIFIC CONCLUSIONS

Based on laboratory results obtained to date coupled with theoretical considerations for biological systems we find the following:

1) PH acts in conjunction with total ammonia level to cause the "un-ionized" (or free) ammonia concentration in solution to act as a master variable influencing nitrification biokinetics. Free ammonia level acts as a substrate inhibitor to nitrification biokinetics, with a maxima in specific nitrification removal rates existing at free ammonia levels of about 10 mg/L.

2) Un-ionized ammonia begins to inhibit nitrification at concentrations greater than 10 mg/L.

3) Suggested sludge ages to maintain effective nitrification when un-ionized ammonia is neither limiting or inhibitory (considering a safety factor of about 2) is

   pH 7.0: 15-18 days
   pH 8.0: 9-12 days
   pH 9.0: 12-15 days

4) Nitrification biokinetics appear very sensitive to elevated temperatures with rates of nitrification increasing to an apparent maxima at 30°C, beyond which the overall rate decreases. This is found to be caused by a decrease in the maximum rate of nitrification (Vmax), a decrease in the observed yield coefficient, and increase in Michaelis-Menten constant (Km) at temperatures in excess of 30°C.

5) Based on theoretical calculations coupled with laboratory experiments, it is suggested that wastewater temperatures be kept below 30°C to assure stable nitrification producing effluents of 10 mg/L ammonia or less.

6) Trace organics have been found to act as toxic inhibitors to nitrification biokinetics. As one example, phenol was found to inhibit the maximum rate of specific ammonia utilization (Vmax) in a manner proportional to the square root of the phenol concentration.

7) Work is continuing in the area of evaluation of the influences of SCN, ethyl pyridine, and other trace substances on the biokinetics of nitrification. It is anticipated that an overall model, or linkages of models may be developed for a better understanding and design of "one-stage" systems for carbonaceous and ammonia removals from coke plant and other phenolic based wastewaters.

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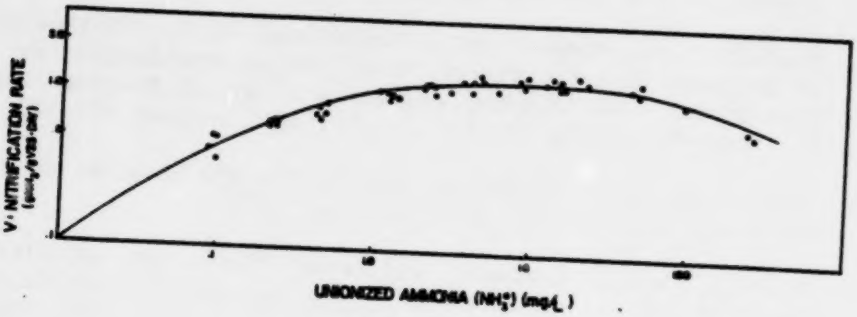
FIGURE 1

AMMONIA UTILIZATION RATE vs UNIONIZED AMMONIA; pH=8.0



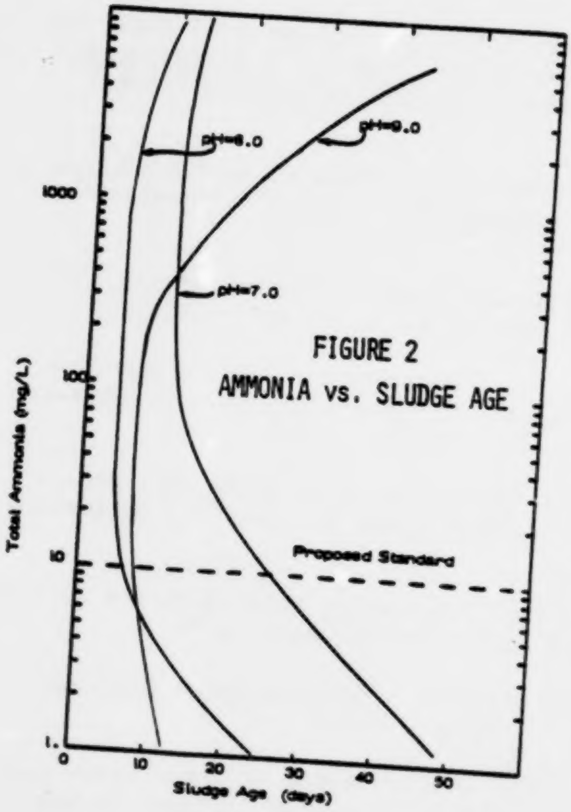


FIGURE 2
AMMONIA vs. SLUDGE AGE

Vmax vs. Temperature

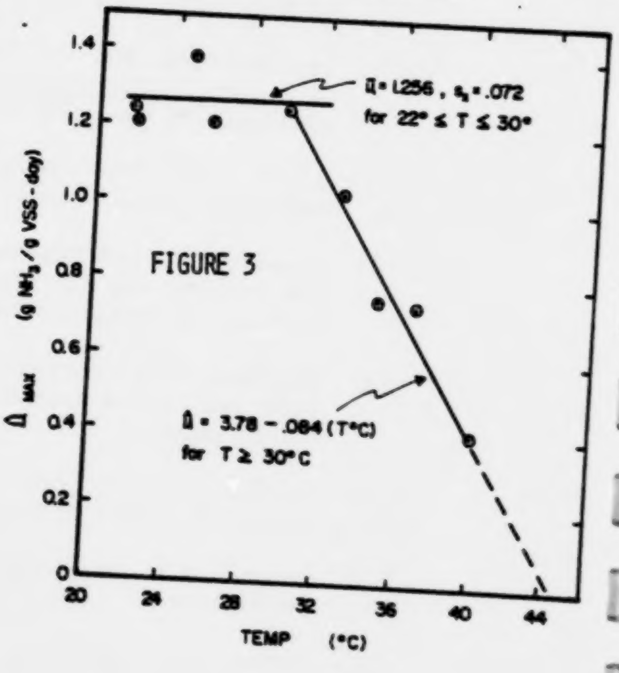


FIGURE 3

Km vs. Temperature

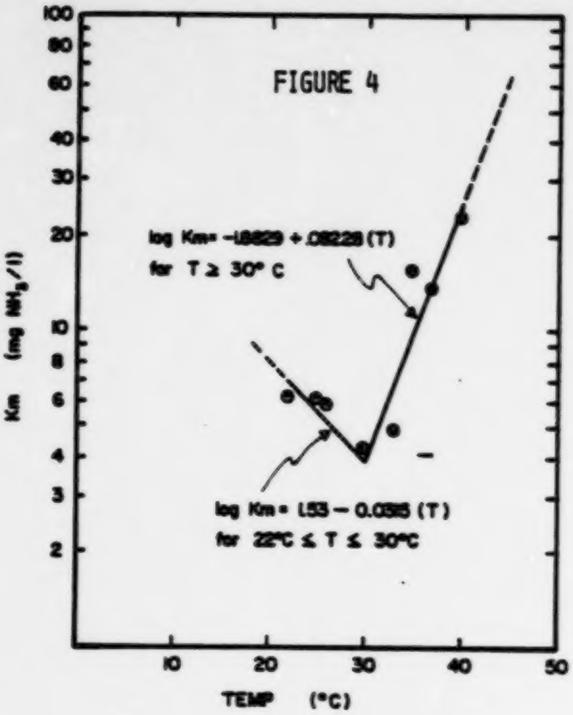


FIGURE 4

Observed Yield Coefficient
vs.
Temperature

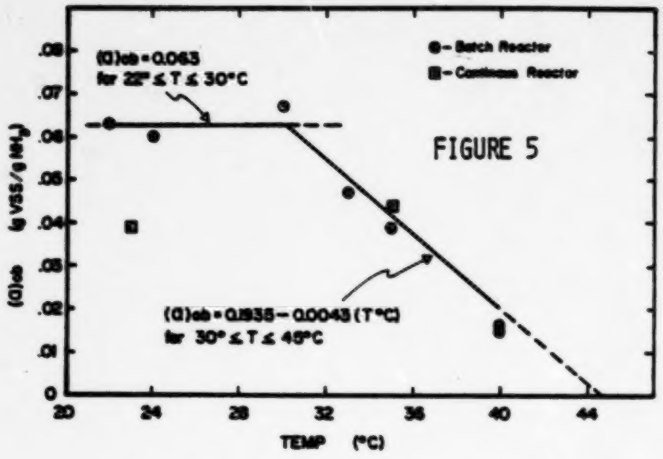


FIGURE 5

Effluent NH$_3$ Concentration
vs.
Sludge Age

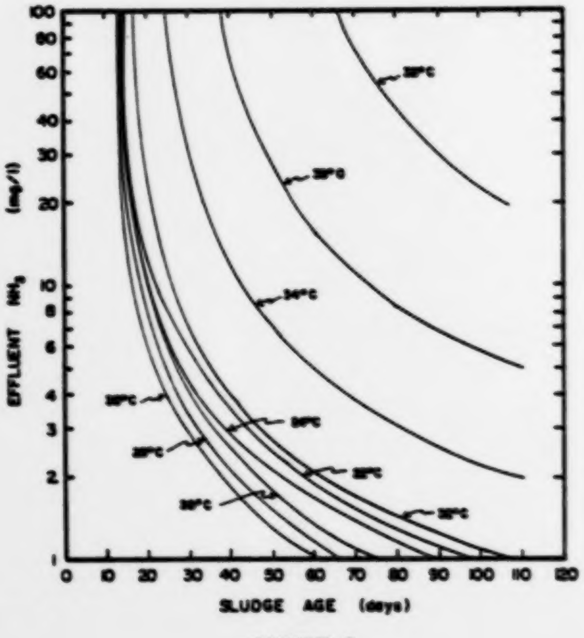


FIGURE 6

Calculated Required Sludge Age
to meet Indicated NH$_3$ Effluents
vs.
Temperature

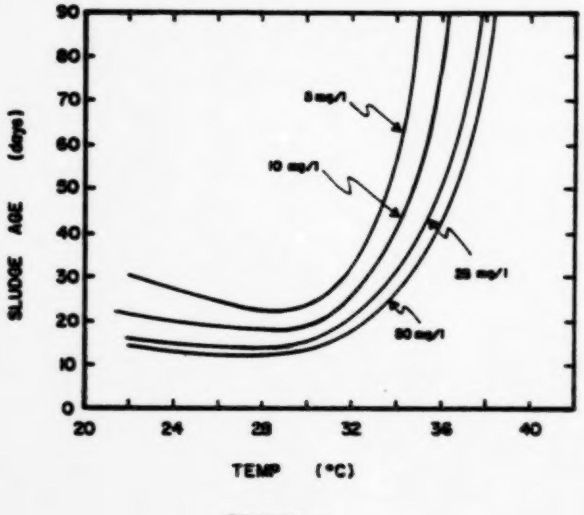


FIGURE 7

FLOTATION OF IRON-CYANIDE COMPLEXES FROM IRON AND COKE PLANT WASTE WATERS

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ABSTRACT

Distribution curves indicate that long chain quaternary amines will complex cyanide, ferrocyanide and ferricyanide. The neutral organometallic complexes formed are hydrophobic because of the long chain alkyl groups of the amine and therefore should be capable of attachment to an air bubble and concentrated in the froth product. This concept was tested on synthetic ferricyanide solutions and to a limited extent on ferrocyanide solutions in a small continuous flotation column. Ferricyanide removal was found to be a function of retention time, initial ferricyanide concentration, mole ratio of amine to ferricyanide, and chloride interference. The air flow rate and solution pH in the range of 4 to 10 had relatively minor effects. Under optimum conditions ferricyanide removals of approximately 80% were achieved in a single stage flotation.

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FLOTATION OF IRON-CYANIDE COMPLEXES

FROM IRON AND COKE PLANT WASTE WATERS

Soluble cyanide species exist in by-product coke plant effluents in concentrations of 7.0 to 110 mg/ℓ of cyanide.[1] The cyanide is present as metallic cyanide complexes, principally ferrocyanide and ferricyanide, as well as free cyanide. The U.S. Environmental Protection Agency (EPA) has issued regulations limiting the discharge of cyanide as given in the BATEA guidelines to 0.25 mg/ℓ. These regulations are scheduled to take effect on July 1, 1985.

Economic removal of the relatively low levels of cyanide in these effluents requires a process capable of high volume treatment at low cost. Flotation processes such as used in the mineral industry meet these requirements. However, in contrast to flotation of fine mineral particles, cyanide removal requires the flotation of an ionic species or microparticulate particles. One possible method of achieving this ionic flotation is to complex the ionic cyanide species with a hydrophobic complexing agent to produce a neutral ion-pair complex capable of attaching itself to an air bubble. Grieves and Bhattacharyya[2] have demonstrated that a cationic surfactant, ethylhexadecylammonium bromide allows removal of ferrocyanide in a batch foam separation process. They also demonstrated that microparticulate iron-ferrocyanide would respond to this reagent.

In the present study the ion flotation of ferricyanide was studied using a quarternary amine surfactant, tricaprylmethylammonium chloride (Aliquat 336, General Mills), in a single stage column flotation process.

COMPLEX FORMATION

In order to determine the ability of the amine to complex cyanide species, distribution tests were run using a chloroform solution containing 1% amine and aqueous solutions of 2.0 mg/ℓ $Fe(CN)_6^{-4}$, 20.0 mg/ℓ $Fe(CN)_6^{-3}$, and 20.0 mg/ℓ CN^- respectively. As shown in Figure 1 the amine extracts all of these ions from the aqueous phase indicating complex formation and therefore the possibility of their removal by flotation.

FLOTATION OF FERRICYANIDE

All flotation tests were carried out in a continuous flotation column using synthetic solutions of $K_3Fe(CN)_6$ containing 36.8 mg/ℓ $Fe(CN)_6^{-3}$. The column had an inside diameter of 4.7 cm and an effective length of 47 cm. A fritted glass disc with a pore size of 25-50 micrometers was used as a gas dispenser. A diagram of the apparatus is shown in Figure 2. The general flotation procedure was to disperse the amine in a small volume of feed solution and add this dispersion to the bulk of the feed in the conditioning tank. After a period of conditioning, usually 10 to 12 minutes, the feed solution was pumped through the column countercurrent to the air flow and the froth product removed. Unless otherwise stated an air flow rate of 0.16 ℓ/min/cm² and a flotation time of 1.74 minutes was used.

The effectiveness of flotation was determined by the fraction removed, Fr, and by the removal factor, RF, as defined below:

$$Fr = (A_f V_f - A_u V_u)/A_f V_f \quad (1)$$

$$RF = 1 - A_u/A_f \quad (2)$$

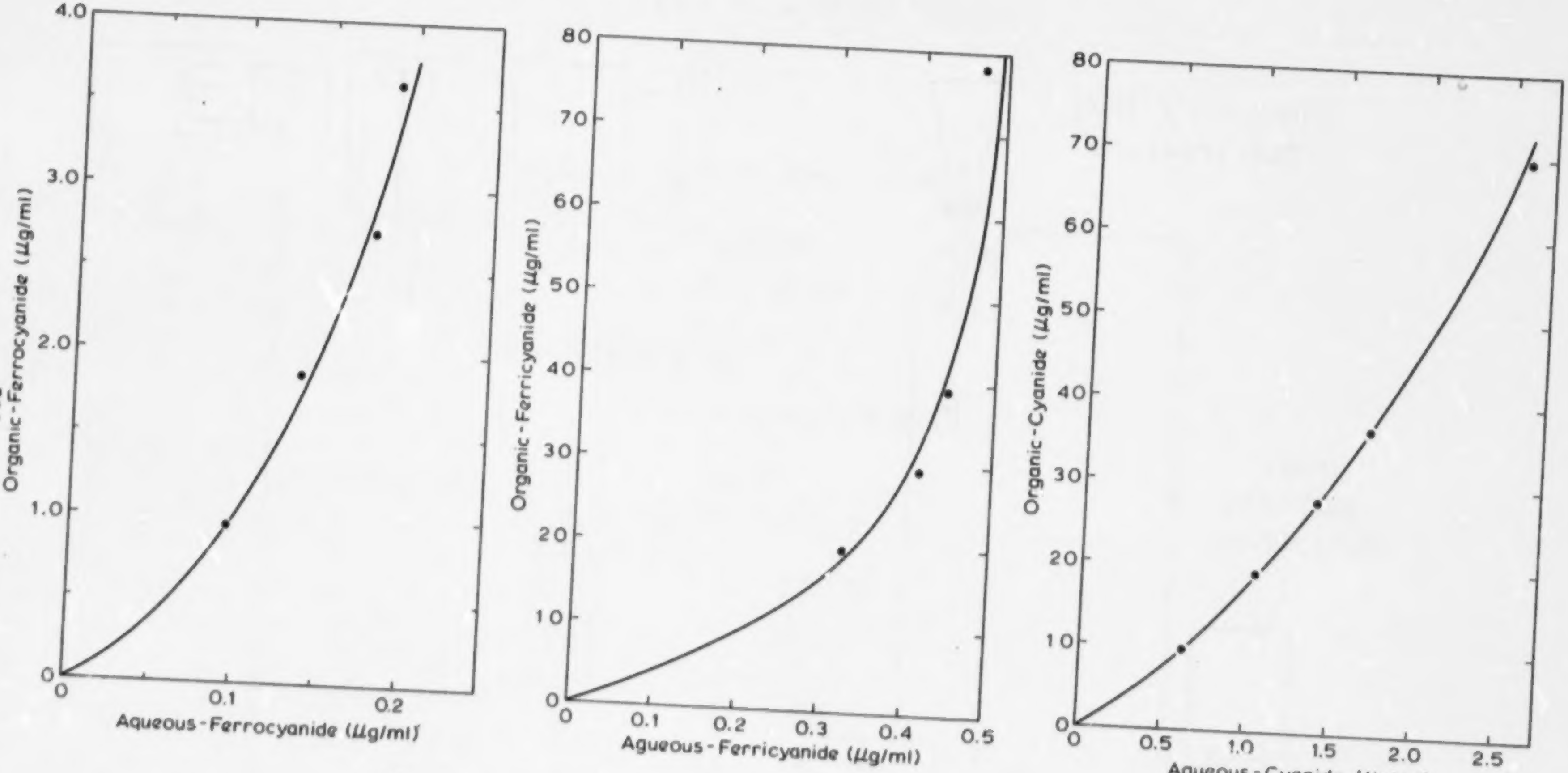

Figure 1. Distribution equilibria for cyanide species.

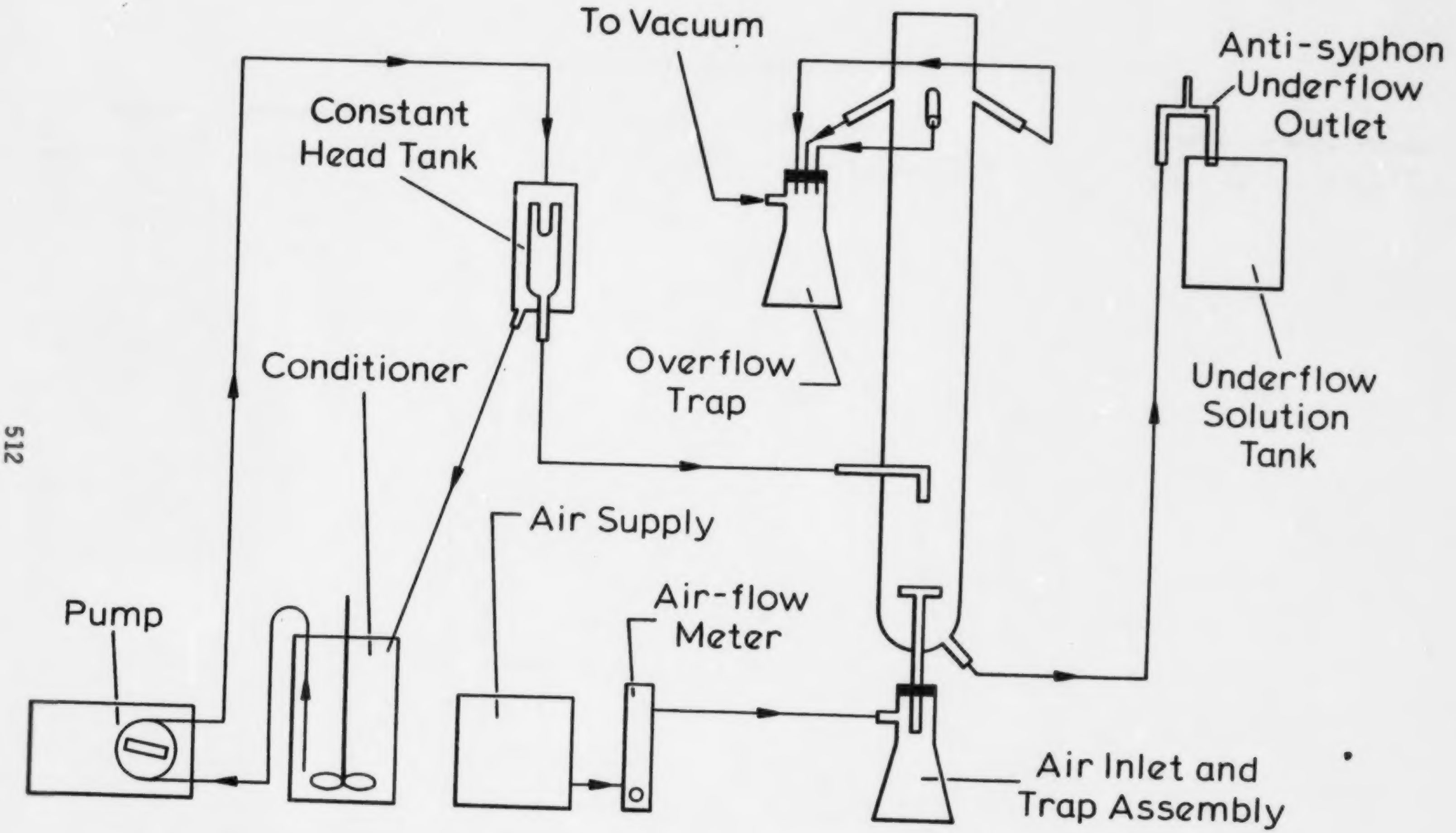

Figure 2. Flotation apparatus.

where A_f and A_u are the cyanide concentrations in the feed and underflow respectively, and V_f and V_u the volumes of the feed and underflow. The fraction removed gives the fraction of total cyanide in the overflow and is a function of the amount of solution carried over in the froth product. The removal factor assumes the overflow solution volume is zero.

Amine Concentration

The overall reaction for complex formation is shown in Equation 3 below:

$$3R_4N\,C\ell + Fe(CN)_6^{-3} = Fe(CN)_6\,(R_4N)_3 + 3\,C\ell^{-1} \tag{3}$$

Therefore the theoretical quantity of amine required to form a neutral complex would be at an amine to ferricyanide mole ratio of 3 to 1. Since this above reaction is an equilibrium reaction, some excess amine would be required to assure essentially complete reaction. Maximum recovery was achieved at an amine-ferricyanide ratio of 3.75 to 1 as shown in Figure 3. The neutral complex formed agglomerates into small wax-like particles and is recovered in the froth product. This amine usage is somewhat higher than the theoretical requirements as might be expected based on equilibrium considerations. At lower ratios the recovery decreases because of insufficient amine. At higher ratios the recovery also decreases. At the high amine ratios, emulsification occurs with a resulting decrease in recovery. This emulsification probably results from adsorption of excess amine on the wax particles with the hydrophilic end of the amine outward resulting in particle repulsion.

Many coke plant waste waters contain relatively high concentrations of chloride. Since the amine is in the chloride form, higher amine concentrations should be required in chloride solutions in order to drive the reaction to the right as indicated in Equation 3. Flotation from solutions containing 5000 mg/ℓ chloride indicate that this occurs as shown in Figure 4. However, in these solutions the recovery does not reach a maximum but continues to increase with increasing amine addition. Emulsification does not occur in these chloride-containing solutions at these higher amine ratios.

Sutherland and Wark[3] have shown that the presence of chloride ion decreases the critical micelle concentration of amines. The polar groups of the amines forming the micelle would be at the surface of the micelle and thus react with the ferricyanide. In addition, by being in this micelle formation, the hydrocarbon end of the amine is not available for adsorption on the wax particles. Consequently no emulsification occurs.

Flotation Variables

Recovery was found to increase rapidly with increasing conditioning time until a steady state was reached at approximately thirteen minutes as shown in Figure 4. It is possible that the conditioning time could be decreased by dissolving the amine in a water soluble solvent such as ethanol prior to addition.

Recovery also increases with increasing flotation time as shown in Figure 5. As indicated the recovery increased from 75% at a flotation time of 1.07 minutes to 83% at a flotation time of 2.3 minutes.

Increasing the air flow rate over a range of 0.08 to 0.22 $\ell/\text{min}/\text{cm}^2$ had only a minor effect on recovery as shown in Figure 6. The sharp decrease in the removal factor at the high air flow rate resulted from excessive carryover of solution into the overflow product.

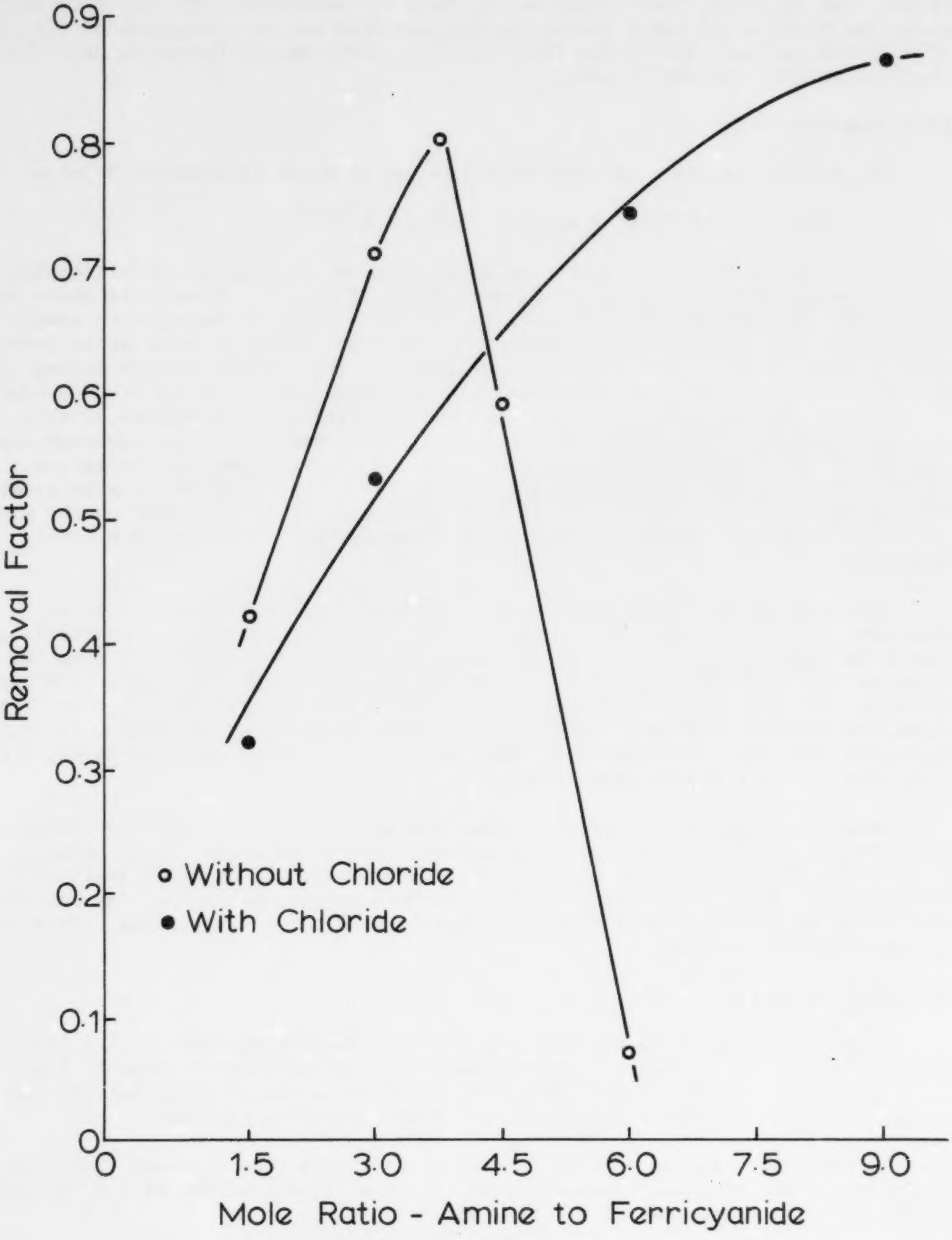

Figure 3. Recovery as a function of amine addition.

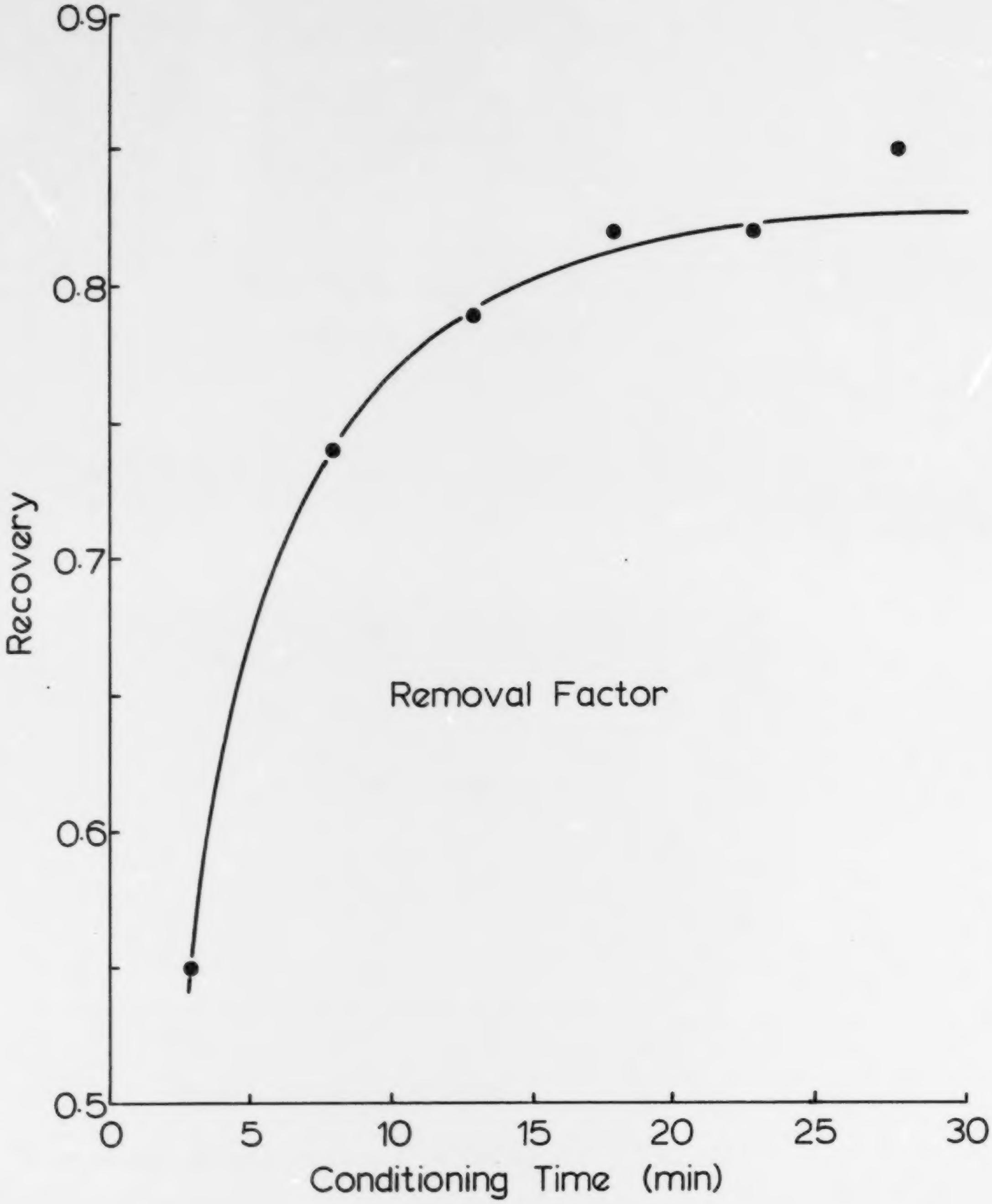

Figure 4. The effect of conditioning time on recovery.

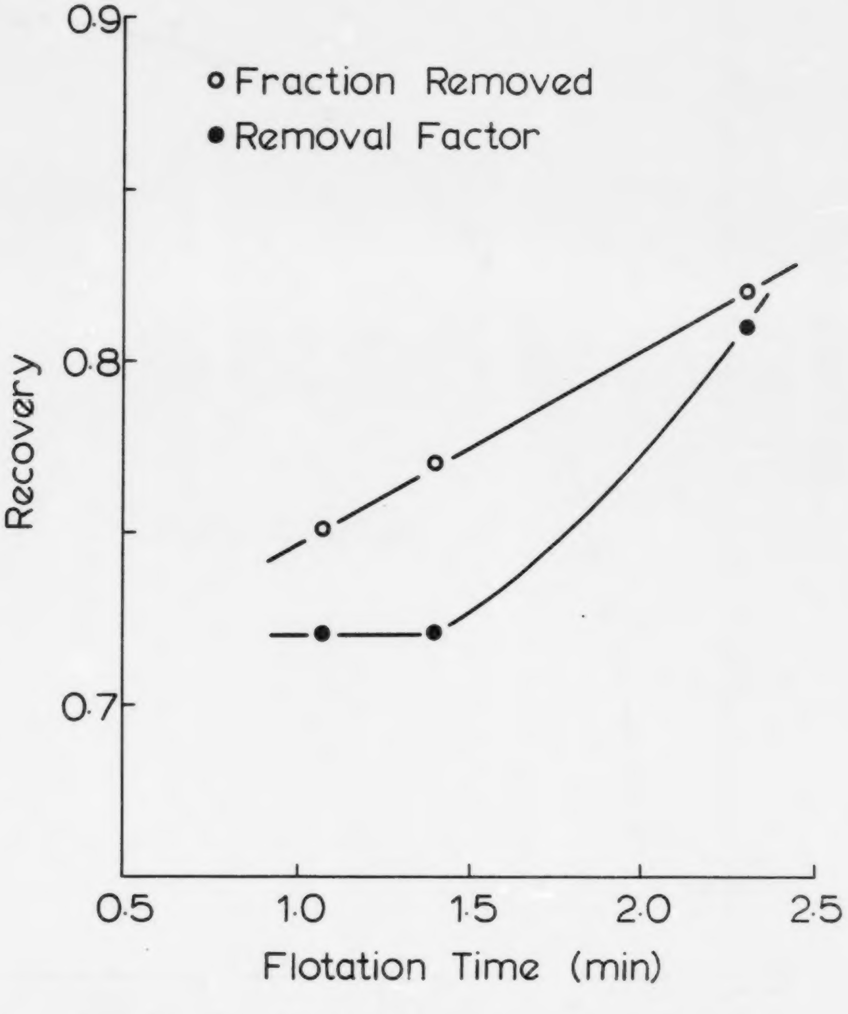

Figure 5. The effect of flotation time on recovery.

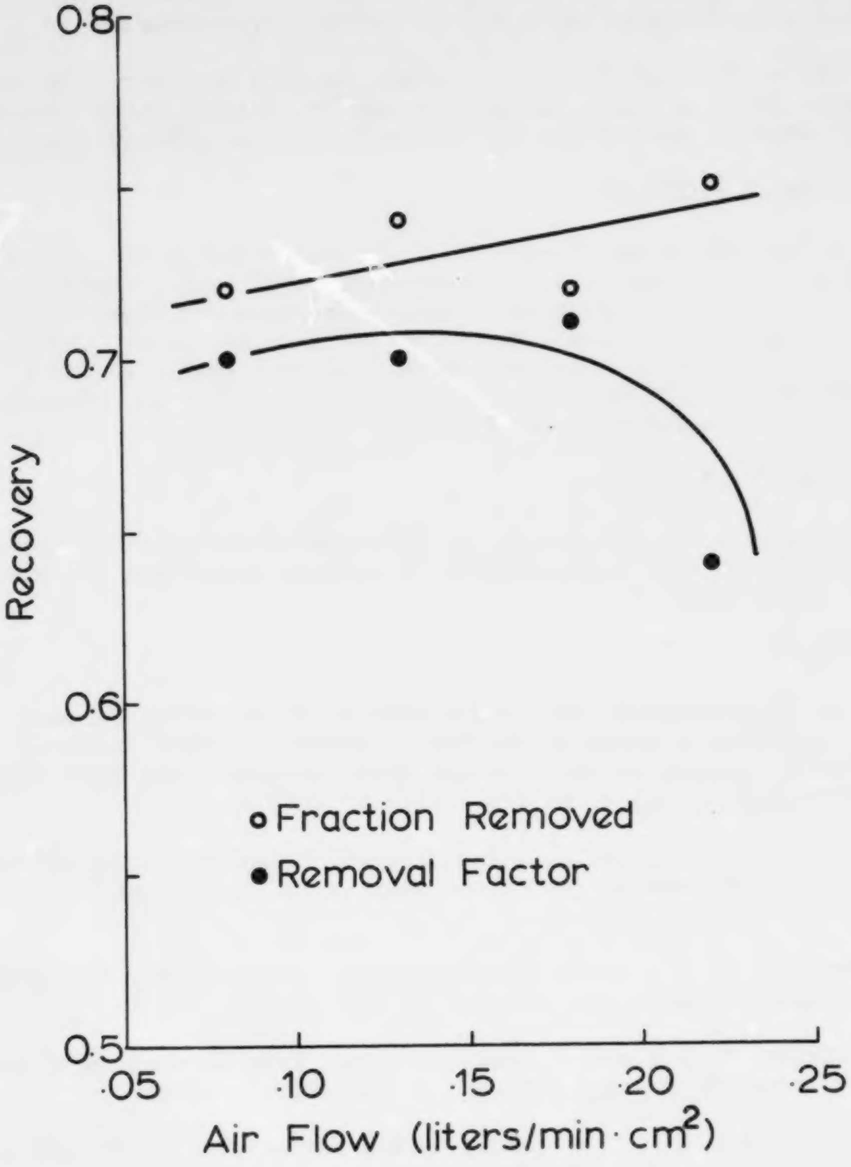

Figure 6. Recovery as a function of air rate.

Solution Variables

Recovery remained essentially constant at about 82% over a ferricyanide concentration range of 30 to 70 mg/ℓ as shown in Figure 7. Below this range the recovery decreased to about 65% at 5.0 mg/ℓ ferricyanide.

The solution pH had little effect on recovery over a pH range of 4 to 7 as shown in Figure 8. The slight decrease in recovery above pH 7 probably results from increased competition for the amine by the hydroxyl ions.

FERROCYANIDE FLOTATION

A limited amount of work on ferrocyanide flotation gave recoveries comparable to that of ferricyanide under comparable conditions. However, complex formation was slower with ferrocyanide. Cyanide ion does not float well at all probably because of ion hydration. However, free cyanide can be converted to ferrocyanide by addition of ferrous sulfate at neutral or slightly acidic pH values. Conversion of free cyanide to ferricyanide is much more difficult. Present work is being directed toward ferrocyanide flotation.

ACKNOWLEDGEMENTS

This work was carried out at Michigan Technological University with the support of the U.S. Environmental Protection Agency and the American Iron and Steel Institute.

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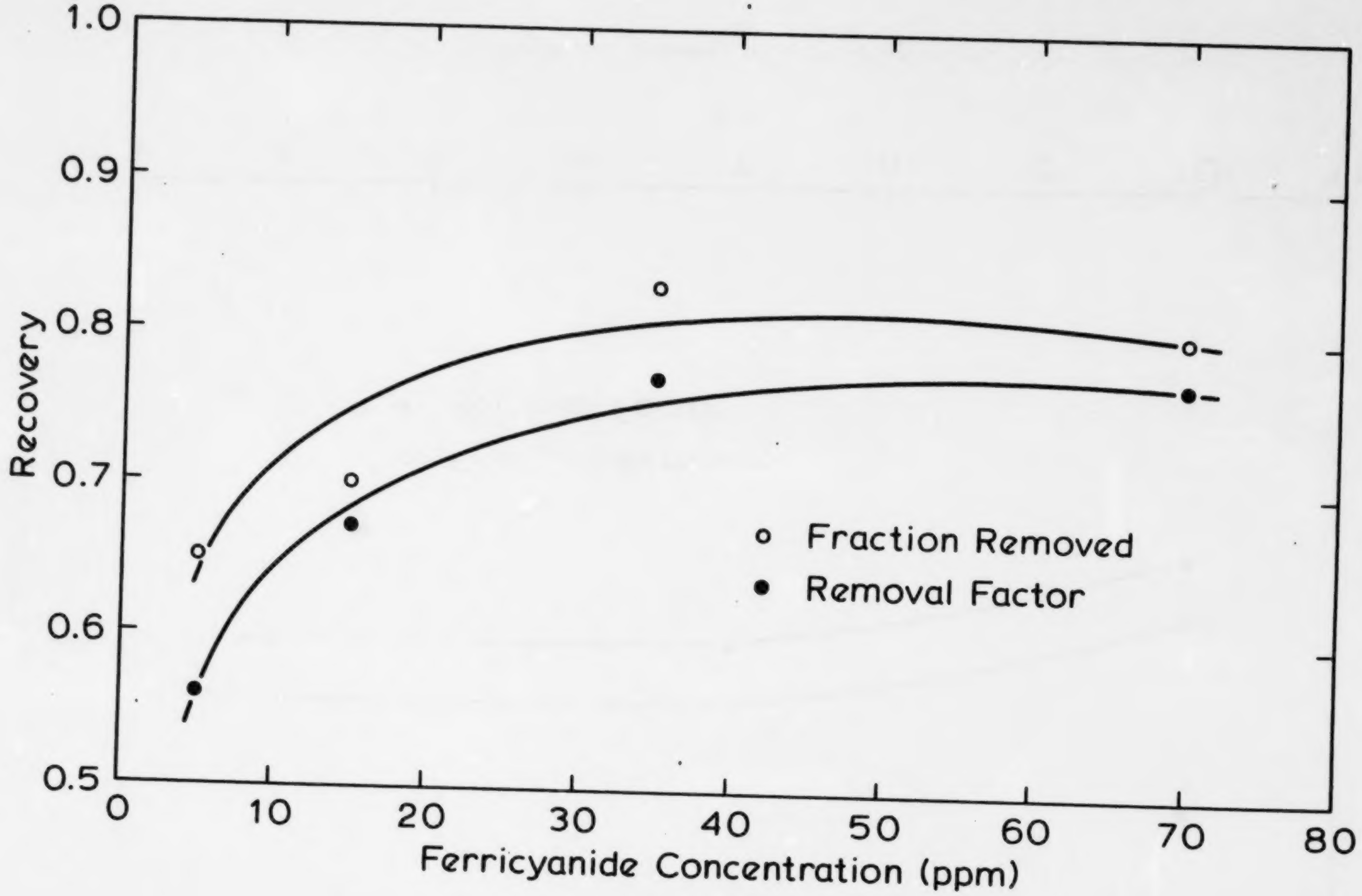

Figure 7. The effect of ferricyanide concentration on recovery.

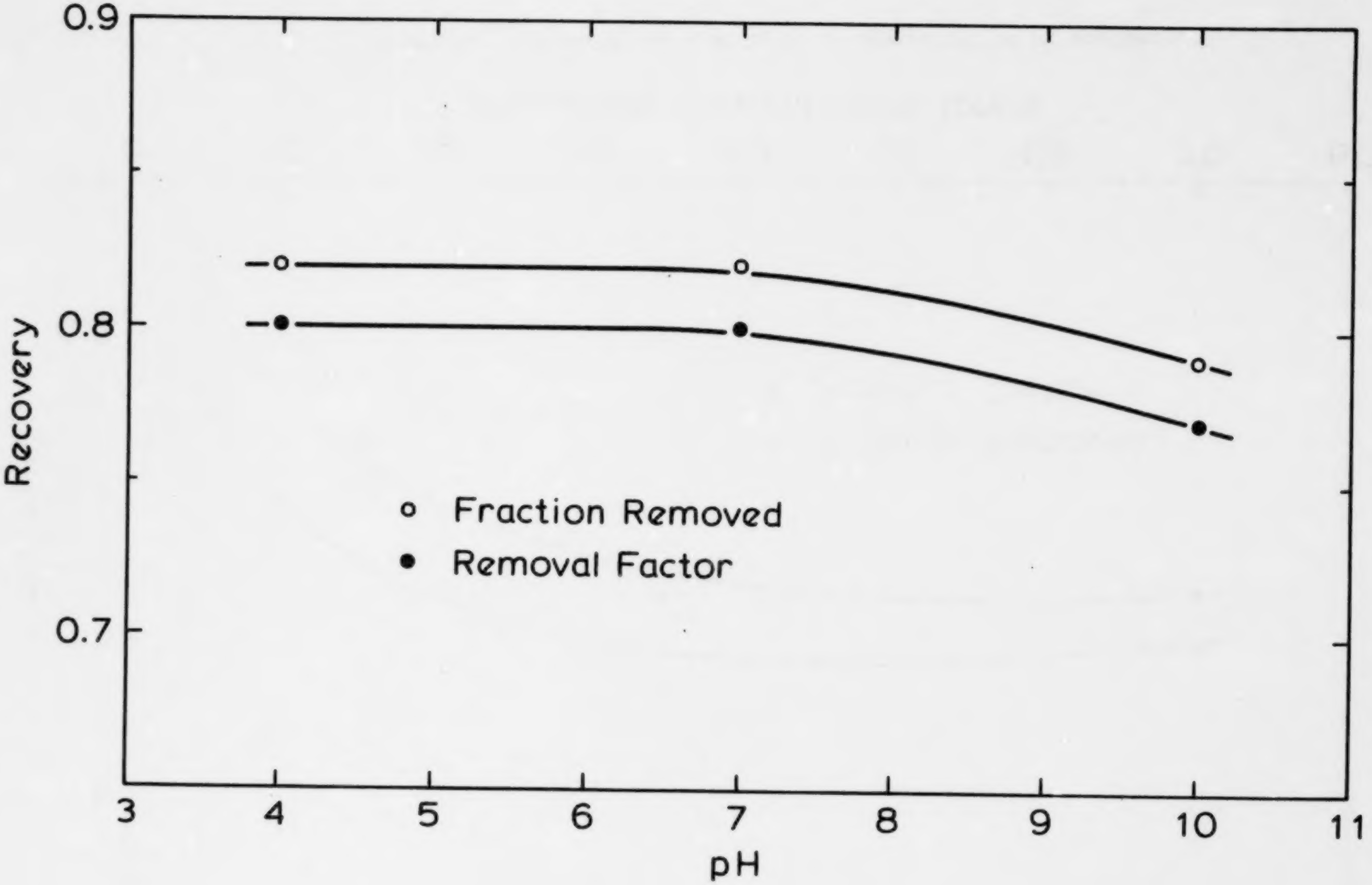

Figure 8. Recovery as a function of pH.

Session 3: SOLID WASTE POLLUTION ABATEMENT

Chairman: John S. Ruppersberger
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

IMPACT OF THE RESOURCE CONSERVATION AND RECOVERY ACT (RCRA) ON THE STEEL INDUSTRY

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and
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RCRA and the Steel Industry

The Resource Conservation and Recovery Act (RCRA) is structured to ensure that our society will view its waste management responsibilities seriously. The failure to realize or predict the consequences of improper waste management in the past have and probably will continue to manifest itself with often tragic incidents. RCRA will have a major effect on how all wastes, whether hazardous or nonhazardous, will be handled in the future.

Nearly 60 million metric tons of solid waste are currently generated each year by the steel industry in the U.S. Approximately 80-90% of this total quantity is probably non-hazardous. Due to commercial sale and/or in plant recovery of over 60% of these solid wastes, approximately 19 million metric tons (excluding rubble) of non-hazardous solid wastes remains to be disposed each year. Table 1 shows the estimated types and quantities of non-hazardous solid waste annually generated.

The steel industry also generates hazardous wastes. Table 2 is a list of some wastes which EPA believes to be hazardous.

This paper gives a description of the regulatory requirements for hazardous and non-hazardous wastes and their expected impact on the steel industry.

Regulation of Hazardous Wastes

EPA's new hazardous waste managment system may not eliminate all of the dangerous sites and problems resulting from our past complacency regarding proper hazardous waste disposal, but the regulations do initiate the establishment of a system which will lead to the proper management of hazardous waste and prevent the creation of new catastrophic situations.

This system is based upon the concept of "cradle-to-grave" management, i.e., tracking the waste from its point of generation to its point of disposal. All generators, transporters, and owner/operators of storage, treatment, and disposal facilities for hazardous waste have responsibilities within this sytem.

Under Subtitle C of the Resource Conservation and Recovery Act, EPA has promulgated six regulations:

RCRA Section	Subject of Regulation	Final Regulation
3001	Identification and Listing of Hazardous Waste	May 19, 1980
3002	Standards for Generators of Hazardous Waste	February 26, 1980
3003	Standards for Transporters of Hazardous Waste	February 26, 1980
3004	Standards for Hazardous Waste Facilities:	
	Phase 1 - Preliminary Facility Standards	May 19, 1980
	Phase 2 - Technical Design Standards	Fall, 1980
3005	Permits for Treatment, Storage, or Disposal Facilities	May 19,1980
3006	Guidelines for Development of State Hazardous Waste Programs	May 19,1980
3010	Notification Process	February 26, 1980

Identification and Listing of Hazardous Waste (3001)

The first major area of the regulations is the identification and listing of hazardous wastes. RCRA defines a hazardous waste essentially as a solid waste that may cause substantial hazard to health or the environment when improperly managed. The Act also instructs EPA to list known hazardous wastes and to establish criteria for the testing of all wastes to determine whether or not they are hazardous.

Characteristics of Hazardous Waste

Hazardous wastes are identified on the basis of measurable characteristics for which standardized tests are available. The principal characteristics that make a waste hazardous are specified levels of:

- ignitability - posing a fire hazard during routine management

Table 1

Estimated Annual Quantities of Non-Hazardous
Solid Wastes Generated by the Steel Industry
(Based on Raw Steel Production of 114 Million Metric Tons) (Ref.1,6)

Waste	Quantity Generated	Waste Dispositions		Quantity Landfilled
	Thousand Metric Tons (dry wgt.)	Percent Recycled/Sold	Percent Disposed	Thousand Metric Tons
Slags				
Blast Furnace	20,850	95%	5%	1,040
Basic Oxygen Furnace	10,200	50%	50%	5,100
Electric Furnace	3,000	20%	80%	2,400
Open Hearth Furnace	4,400	25%	75%	3,300
	38,450	69%	31%	11,840
Scales				
Soaking Pit	1,000	---	100%	1,000
Primary Mill	4,600	80%	20%	920
Continuous Casting	100	80%	20%	20
Rolling Mills	700	80%	20%	140
	6,400	67%	33%	2,080
Sludges				
Blast Furnace	1,800	75%	25%	450
Basic Oxygen Furnace[1]	800	25%	75%	600
Rolling Mills	275	---	100%	275
Plating, Galvanizing	100	100%	---	---
	2,975	56%	44%	1,325
Dusts				
Blast Furnace	1,200	85%	15%	200
Basic Oxygen Furnace[2]	400	25%	75%	300
Open Hearth Furnace	250	15%	85%	200
	1,850	55%	45%	700
Miscellaneous				
Fly Ash/Bottom Ash[3]	250	---	100%	250
Rubble	3,400	---	100%	3,400
	3,050	0%	100%	3,650

[1] 64% of BOF's utilize wet emission controls, 35% utilize dry controls. Dust in the form of kish will be generated whichever device is utlized.

[2] Since 90% of electric furnaces utilize dry controls, assume dry controls are used solely.

[3] Assume (a) 2.5 million metric tons of coal consumed (b) ash content of coal is 12%.

Table 2

Estimated Annual Quantities of Hazardous Solid Wastes Generated by the Steel Industry(Ref.2)

Waste	Quantity Generated	Percent Disposed
Decanter Tank Tar Sludge	65,000 metric tons	55%
Ammonia Still Lime Sludge	870,000 metric tons	85%
Electric Furnace Dust/Sludge	340,000 metric tons	100%
Spent Pickle Liquor	1.4 billion gallons	40%
Sludge from Lime Treatment of Spent Pickle Liquor[1]	5 million metric tons	100%
Spent Halogenated Solvents and Recovery Sludges/Still Bottoms	20,000 metric tons	100%

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[1] Assumes treatment of all spent pickle liquor.

- corrosivity - ability to corrode standard containers, or to dissolve toxic components of other wastes
- reactivity - tendency to explode under normal management conditions, to react violently when mixed with water, or to generate toxic gases
- EP toxicity - (as determined by a specific extraction procedure) - presence of certain toxic materials at levels greater than specified in the regulation.

List of Hazardous Wastes

Wastes that possess any of the four hazardous waste characteristics or that meet the criteria for general toxicity have been included in the hazardous waste listing. The waste listing is composed of several sections: specific wastes, waste sources, and waste processes.

General toxicity is defined as characteristic of waste which contain one or more constituents that have been found to have toxic effects on humans or other life forms. EPA can also consider other factors to determine if the waste may cause or potentially cause "substantial" hazard to human health or the environment. The other factors which EPA may consider are:

- the degree of toxicity of the toxic constituents of the waste;
- the concentration of these constituents in the waste;
- the potential for these constituents or their by-products to migrate from the waste into the environment;
- the persistence and degradation potential of the constituents or their toxic by-products in the environment
- the potential for the constituents or their toxic by-products to bioaccumulate in ecosystems;
- the plausible and possible types of improper management to which the waste may be subjected;
- the quantities of the waste generated;
- the record of human health and environmental damage that has resulted from past improper management of wastes containing the same toxic constituents.

It is possible for the generator to get an exemption from regulation even if the waste is listed in the regulation. The regulation includes delisting procedures for generators to follow if they believe their facility's individual waste is fundamentally different from the waste listed. The generator must demonstrate, or reference test data that demonstrate, that the specific waste does not meet the criteria which caused the Agency to list the waste. This provision allows flexibility recognizing that individual waste streams vary depending upon raw materials, industrial processes, and other factors.

Excluded Wastes

Certain wastes are not subject to RCRA Subtitle C hazardous waste controls. Some of the wastes excluded and applicable to the steel industry include:

- industrial wastewater discharges that are point source discharges subject to regulation under Section 402 of the Clean Water Act, as amended;
- wastes that are reused or recycled, except for the storage and transportation of sludges and listed wastes;
- fly ash, FGD sludge, bottom ash from combustion of coal or other fossil fuels.

Generator (3002):

The regulations (40 CFR Part 262) issued under section 3002 of RCRA require a generator of hazardous waste to determine if his waste is hazardous.

This determination may be made via one of the following means:

(1) a waste may be listed by EPA as being hazardous;

(2) if not listed, the waste may be tested by the generator against the characteristics for determining hazardousness;

(3) the generator may declare the waste to be hazardous based upon his knowledge of the materials or processes used in generating the waste.

Additionally a generator is required to:

- obtain an EPA identification number
- obtain a facility permit if the waste is accumulated on the generator's property more than 90 days
- use appropriate containers and label them properly for shipment
- prepare a manifest for tracking hazardous waste

- assure, through the manifest system, that the waste arrives at the designated facility
- submit an annual summary of activities.

Once a solid waste is determined to be hazardous, it is subject to all of the controls under Subtitle C and the generator transporters, storers, treaters, and disposers of the waste are deemed responsible to meet the applicable requirements.

Manifest

The major mechanism for tracking and controlling hazardous waste is the manifest system. A generator of hazardous waste is responsible for preparation of a manifest containing:

- name and address of the generator;
- names of all transporters;
- name and address of the permitted facility designated to receive the waste. (An alternate facility may be designated if an emergency prevents use of the first facility);
- EPA identification numbers of all who handle the waste;
- U.S. Department of Transportation (DOT) description of the waste;
- quantity of waste and number of containers;
- the generator's signature certifying that the waste has been properly labeled, marked, and packaged in accordance with DOT and EPA regulations.

The owner/operator of the facility receiving the waste is responsible for verifying delivery of the waste and returning a copy of the manifest to the generator.

Transporters (3003)

The regulation for transporters of hazardous waste (40 CFR Part 263) was developed jointly by EPA and the U.S. Department of Transportation (DOT). The EPA regulation on transporters incorporates by reference pertinent parts of DOT's rules on labeling, marking, packaging, placarding, and other requirements for reporting hazardous discharges or spills during transportation. DOT, in turn, is amending its regulations on transportation of hazardous materials to include EPA's requirements.

The regulation (Part 263) requires a transporter of hazardous waste to:

- obtain an EPA identification number;
- comply with the manifest system for tracking hazardous waste;
- deliver the entire quantity of hazardous waste to the facility designated by the generator on the manifest
- retain a copy of the manifest for 3 years;
- comply with DOT regulations pertaining to reporting of discharges or spills;
- clean up any hazardous waste discharged during transportation.

Facility Standards (3004)

Owners and operators of facilities that treat, store, or dispose of hazardous waste must comply with the standards promulgated under section 3004 of RCRA (40 CFR Parts 264 or 266). The regulations under this section, which set standards for hazardous waste facilities, serve a threefold purpose:

- to establish proper treatment, storage, and disposal practices;
- to provide States with minimum standards in order to receive EPA approval (required under section 3006 of RCRA) of their hazardous waste programs;
- to provide the technical basis for EPA-issued facility permits (required under section 3005 of RCRA) in States that do not operate a RCRA program.

EPA is promulgating standards for hazardous waste facilities in two phases. Phase I - Interim Status Standards (in the spring of 1980) provide facilities with temporary authority to continue their operations, upon notifying EPA and obtaining an identification number. This temporary authority will be effective until promulgation of the Permanent Status Standards.

"Interim status" gives hazardous waste facilities temporary authority to continue operations pending final administrative action on facility permit applications (required under RCRA Section 3005). Of course, until the permit decision is made, all hazardous waste facilities must meet the conditions of the Interim Status Standards as stated in the May 19, 1980 Federal Register - Final Hazardous Waste Regulations. Facility owners and operators who qualify for interim status are treated as having a permit during this period. To qualify for interim status, a facility must have been in existence (in operation or under construction) on November 19th.

Interim Status Standards are designed to ensure adequate operating practices and closure and post closure activities. Requirements for interim status are largely managerial--they do not include financial assurance or design and operating standards required for a facility permit. These standards will soon be promulgated as Phase II.

Interim Status Standards (Part 265) for nonpermitted facilities, promulgated as Phase I in spring 1980, include:

1. Administrative and nontechnical requirements:

    - General

        -- waste analysis: detailed chemical and physical analyses, waste analysis plan, specific requirements for each facility type

        -- security: artificial or natural barrier with controlled entry or 24-hour surveillance, and warning signs

        -- inspection: inspection plan and log; remedy of any deterioration, malfunction, or imminent hazard

    - Personnel training

        -- classroom or on-the-job training, annual review of initial training, records on personnel training

    - Preparedness and prevention

        -- alarm system and emergency equipment; access to same

        -- arrangements with local emergency authorities

    - Contingency plan, emergency procedures, and emergency coordinator

    - Manifest system procedures

    - Operation records of activities required by the regulation, such as manifest information, waste analyses records, testing and analytical data, and demonstration reports for variances

    - Reporting requirements, such as annual reports and unmanifested waste reports.

2. General facility requirements (Phase I):

   - General operation requirements
   - Special requirements for ignitable, reactive, and incompatible wastes
   - Ground-water monitoring (monitoring system to be in operation by November 1981)
   - Closure and postclosure plans: estimate of costs and description of how facility will be closed, notice of facility closure, and postclosure monitoring and maintenance

3. Specific facility requirements:

   - Disposal of liquids in landfills or containers
   - Control of runoff from waste piles, land treatment, and landfills (controls to be in operation by November 1981)
   - Land treatment facilities monitoring and restrictions on growing foodchain crops
   - Incinerators and treatment facilities
   - Underground injection

Permanent Status Standards (Part 264) for permitted facilities, will soon be promulgated as Phase II.

General facility requirements will include technical, monitoring, closure and postclosure, and financial requirements. The facility permit regulation under section 3005 of RCRA becomes effective and processing of permit applications begins at this time.

Further technical requirements will be promulgated by EPA intermittently over a period of years. These will include resolution of complex technical issues and reproposal and promulgation of more definitive Phase II standards, for example, specific design or operating standards for landfills. The technical refinements may also include standards for specific industries and wastes which require tailored standards.

Facility Permits (3005)

The regulation promulgated under section 3005 of RCRA (40 CFR Parts 122 and 124) requires that any person who owns, operates, or proposes to own or operate a facility that treats, stores, or disposes of hazardous waste receive a permit from EPA or a State authorized to conduct its own hazardous waste program. Most requirements in the regulation are only applicable where EPA issues permits; selected portions apply to authorized State programs.

Consolidated Permit Program

EPA issues permits for controlling environmental problems under a number of laws. To facilitate and streamline the regulatory process, EPA has consolidated procedures and requirements for the hazardous waste management program with four other programs it administers:

- the Underground Injection Control (UIC) program under the Safe Drinking Water Act
- the National Pollutant Discharge Elimination system (NPDES) under the Clean Water Act
- the Dredge or Fill (section 404) Program under CWA
- the Prevention of Significant Deterioriation (PSD) Program under the Clean Air Act where this program is operated by EPA.

A facility seeking more than one permit is encouraged to consolidate application.

Exclusions

Certain facilities handling hazardous waste do not require a RCRA permit:

- generators who accumulate hazardous waste on-site for less than 90 days
- persons who own or operate facilities solely for the treatment, storage, or disposal of certain hazardous waste excluded from regulation.

Applying for a Permit

Any person who now owns or operates a hazardous waste facility, or who plans to in the future, must apply for a permit. This requirement applies to all existing facilities, facilities in operation or an intermittent basis, or facilities which commenced construction as late as yesterday, November 19. The application is in two parts:

- Part A, which defines the processes to be used; the design capability; and the hazardous waste to be handled. For existing facilities, Part A must be submitted within 6 months of promulgation of the regulation identifying hazardous waste.

- Part B, which contains more detailed information intended to establish that the facility can meet the technical standards promulgated under RCRA section 3004. For existing facilities, Part B must be submitted at a date set by the Regional Administrator.

For proposed new facilities, both Part A and Part B must be submitted at least 180 days before physical construction is scheduled to begin.

If notification is filed with EPA and Part A of the permit application is submitted on time, an existing facility achieves interim status and is considered to have a permit until Part B is acted upon. Obviously, EPA will not be able to issue thousands of hazardous waste permits in less than several years. If approved by EPA, a permit with a term of not more than 10 years will be granted. Meanwhile, the facility must comply with Interim Status Standards promulgated under RCRA section 3004.

State Programs (3006)

Congress clearly prefers that States assume responsibility for controlling hazardous wastes within their borders. Federal financial assistance is available from EPA to States for developing their programs. Section 3006 of the Act specifically provides for States to operate their own hazardous waste programs in lieu of the Federal program, after the authorization by EPA. In States whose programs do not meet the minimum requirements under RCRA, or who do not apply for authorization, EPA must administer the program.

The regulation issued under section 3006 of RCRA (40 CFR Part 113) establishes minimum requirements for State hazardous waste programs in order to receive EPA approval. The regulation is designed to assure consistency in hazardous waste management from State to State.

RCRA generally directs that to receive EPA "final" approval State hazardous waste programs must be "equivalent to and consistent with" the Federal program. "Equivalent" is interpreted to mean "equal in effect." Thus, the regulations provide minimum requirements, with the States allowed to set more stringent standards. Another important element is that States may not impose any requirement that might interfere with the free movement of hazardous wastes across State boundaries to treatment, storage, or disposal facilities holding a RCRA permit.

State programs that are "substantially equivalent" to the Federal program may receive interim authorization, then be gradually upgraded until they qualify for "final" or "full" authorization.

Notification Process (3010)

The control system starts when those engaged in generating, transporting, treating, storing, or disposing of hazardous waste notify EPA as required by section 3010 of RCRA. After receiving notification, EPA assigns an identification number to the notifier. Anyone engaged in transporting, treating, storing, or disposing of hazardous waste who does not notify EPA during the 90-day period following the promulgation of the regulation identifying hazardous waste may not begin or continue operation after the effective date of the regulation without obtaining an EPA identification number.

The regulation issued under section 3010 of RCRA requires that:

- anyone who generates or transports hazardous waste or owns or operates a facility that treats, stores, or disposes of hazardous waste must notify EPA.
- a new generator or transporter must apply to EPA for an identification number before any hazardous waste can be transported. Application for an identification number must be made on the notification form.
- an owner/operator of a site that conducts more than one hazardous waste activity (for example, generation and disposal) may file a single form to cover all activities at that site.
- an owner/operator of more than one site must file a form for each site.

This hazardous waste management system is a new and complex plan which can and will work only if everyone involved with hazardous waste assumes his responsibilities.

Steel Industry Hazardous Waste

As of today, there are four specific source and a number of non-specific source types of wastes associated with the steel industry which have been determined by EPA to be hazardous wastes (as listed in the Federal Register of May 19 and July 16, 1980).

The five specific source wastes are:

(1) Ammonia still lime sludge from coking operations;

(2) Decanter tank tar sludge from coking operations;

(3) Spent pickle liquor from steel finishing operations;

(4) Emission control dust/sludge from the primary production of steel in electric furnaces.

The above wastes were listed as hazardous due to their toxic and/or corrosive characteristics. A summary of the reasons for listing each of these wastes follows:[2]

A. Coking

1. Ammonia still lime sludge from coking operations (T) 5/19/80

   a. These sludges contain the hazardous constituents cyanide, naphthalene, phenolic compounds, and arsenic which adhere to the lime flocs and solids in significant concentrations.

   b. Cyanide and phenol leached in significant concentrations from an ammonia still lime sludge waste sample which was tested by a distilled water extraction procedure. Although no leachate data is currently available for naphthalene and arsenic, the Agency strongly believes that, based on constituent solubilities, the high concentration of these constituents in the wastes, and the physical nature of the waste, these two constituents are likely to leach from the wastes in harmful concentrations when the wastes are improperly managed.

   c. It is estimated that a very large quantity, 963,000 tons (1), of ammonia still lime sludge (5% solids by weight) is currently generated annually, and that this quantity will gradually increase to 1.45 million tons (5% solids by weight) per year as the remaining coke plants add fixed ammonia removal capability to comply with BPT limitations. There is thus the likelihood of large-scale contamination of the environment if these wastes are not managed properly.

   d. Coke plant operators generally dispose of these sludges on-site in unlined sludge lagoons or in unsecured landfill operations. These management methods may be inadequate to impede leachate migration.*

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* Although no data on the corrosivity of ammonia still lime sludge are currently available, the Agency believes that these sludges may have a pH greater than 12.5 and may, therefore, be corrosive. Under §262.11, generators of this waste stream are responsible for testing their waste in order to determine whether their waste is corrosive or would meet any of the other hazardous waste characteristics.

2. Decanter tank tar sludge from coking operations (T) 7/16/80

a. The tank tar-sludge contains significant concentrations of phenol and naphthalene. Phenol is highly toxic. Naphthalene is also toxic and is a demonstrated neoplastic substance in experiments done on laboratory animals.

b. Phenol has leached in significant concentration from a waste sample tested in a distilled water extraction procedure. The Agency believes that, due to the presence of naphthalene in the tar in high concentrations and due to its relative solubility, napthalene also may leach from the waste in harmful concentrations if the waste is improperly managed.

c. These tar-sludges are often land disposed in on-site landfills or dumped in the open. These methods may be inadequate to impede leachate migration and resulting groundwater contamination.

B. Steel Finishing

1. Spent Pickle Liquor (C, T) 5/19/80

a. Spent pickle liquor is corrosive (has been shown to have pH less than 2), and contains significant concentrations of the toxic heavy metals lead and chromium.

b. The toxic heavy metals in spent pickle liquor are present in highly mobile form, since it is an acidic solution. Therefore, these hazardous constituents are readily available to migrate from the waste in harmful concentrations, causing harm to the environment.

c. Current waste management practices of untreated spent pickle liquor consists primarily of land disposal either in unlined landfills or unlined lagoons which may be inadequate to prevent the migration of lead and chromium to underground drinking sources. Treatment of the spent pickle liquor by neutralization is also commonly practiced by the industry in which case, a lime treatment sludge is generated.

d. A very large quantity (approximately 1.4 billion gallons of spent pickle liquor) annually. Thus, there is greater likelihood of large-scale contamination of the environment if these wastes are not managed properly.

e. Damage incidents have been reported that are attributable to the improper disposal of poorly treated spent pickle liquor.

2. Spent Pickle Liquor - Lime Treatment Sludge

It should be noted that the waste "sludge from lime treatment of spent pickle liquor from steel finishing operation" has been removed from the list of hazardous wastes. Several comments indicate that this waste may not be hazardous, particularly if the lime treatment process is conducted effectively. At the same time, however, insufficient data was submitted to warrant a conclusion that these wastes will typically and frequently not be hazardous. Our concern is that these wastes derive from a hazardous waste (spent pickle liquor from steel finishing) which may contain high concentrations of lead and chromium. These heavy metals not only will be present in the sludge, but will be found there in even more concentrated form.

Under these circumstances, we have decided that these waste sludges still should be regulated as hazardous, but to delete these wastes from the hazardous waste list, and instead to rely in the provisions of §261.3 to bring these wastes within the hazardous waste management system. Since these lime treatment sludges are generated from the treatment of a listed hazardous waste (spent pickle liquor), they are considered to be hazardous wastes (§261.3(c)(2)). Further, they remain hazardous wastes until they no longer meet any of the characteristics of hazardous waste and are de-listed (§261.3(d)(2)).

C. Electric Furnace Production of Steel

1. Emission Control dust/sludge from the primary production of steel in electric furnace (T) 5/19/80

a. The emission control dusts/sludges contain significant concentrations of the toxic metals chromium, lead, and cadmium.

b. Lead, chromium and cadmium have been shown to leach in harmful concentrations from waste samples subjected to both a distilled water extraction procedure and the extraction procedure described in the Subtitle C regulations.

c. A large quantity of these wastes (a combined total of approximately 337,000 metric tons) is generated annually and is available for disposal. There is thus likelihood of large scale contamination of the environment if these wastes are mismanaged.

d. The wastes typically are disposed of by being dumped in the open, either on-site or off-site, thus posing a realistic possibility of migration of lead, cadmium, and chromium to underground drinking water sources. These metals persist virtually indefinitely, presenting the serious threat of long-term contamination.

e. Off-site disposal of these wastes will increase the risk of mismanagement during transport.

In addition to the specific source wastes listed above, a number of other wastes (from non-specific sources) which may be associated with some steel industry operations have also been listed as hazardous wastes. These wastes are:

- The following spent halogenated solvents used in degreasing: tatrachloroethylene, trichloroethlene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbon; and sludges from the recovery of these solvents in degreasing operation.

- The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylne, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, and trychlorofluoromethane; and the still bottoms from the recovery of these solvents.

- The following spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone and methanol; and the still bottoms from the recovery of these solvents.

- The following spent non-halogenated solvents: cresols and cresylic acid and nitrobenzene; and the still bottoms from the recovery of these solvents.

- The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol and pyridine; and the still bottoms from the recovery of these solvents.

- Quenching bath sludge from oil baths from metal heat treating operations.

- Spent solutions from salt bath pot cleaning from metal heat treating operations.

- Quenching wastewater treatment sludges from metal heat treating operations.

These wastes were listed as hazardous due to toxicity, ignitibility, or reactivity characteristics. A brief listing summary[2] follows:

A. Wastes From Usage of Halogenated Hydrocarbon Solvents in Degreasing Operations

1. The following spent halogenated solvents used in degreasing: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; and sludges resulting from the recovery of these solvents in degreasing operations (T) - 5/19/80

For all of the listed waste solvents, the listing is based on the following considerations:

a. The chlorinated waste hydrocarbons are toxic and, in some cases, genetically harmful, while chlorofluorocarbons may remove the ozone layer following environmental release.

b. Many steel facilities dispersed throughout the country use halogenated solvents and generate these wastes. Halogenated hydrocarbons from these facilities are either disposed of annually in landfills or by open-ground dumping, either as crude spent solvents or as sludges. Current waste management practices have resulted in environmental damage. Damage incidents serve to illustrate that the mismanagement of these wastes does occur and can result in substantial environmental and health hazards.

c. Since a large majority of the spent solvents and sludges are in liquid form and are highly soluble, the potential for these wastes to migrate from land disposal facilities is high. Spent halogenated solvents can leach from the waste to effect adversely human health and the environment through the resulting contamination of groundwater.

B. Wastes From Usage of Organic Solvents

1. The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene and trichlorofluoromethane; and the still bottoms from the recovery of these solvents (T) - 5/19/80

2. The following spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether,

methyl isobutyl ketone, n-butyl alcohol, cyclohexanone and methanol; and the still bottoms from the recovery of these solvents (I) - 5/19/80

3. The following spent non-halogenated solvents: cresols and cresylic acid and nitrobenzene, and the still bottoms from the recovery of these solvents (T) - 5/19/80

4. The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol and pyridine; and the still bottoms from the recovery of these solvents (I, T)

Wastes resulting from usage of organic solvents typically contain significant concentrations of the solvent. The basis for listing[2] the above wastes as hazardous is:*

a. Each solvent exhibits one or more properties (i.e., ignitability and/or toxicity) which pose a potential hazard.

b. The nine spent solvents listed for meeting only the ignitability characteristic all have a flash point below 60°C (140°F) and are thus considered hazardous.

The solvents listed as either toxic or toxic and ignitable pose a further hazard to human health and the environment. If improperly managed, these solvents could migrate from the disposal site into ground and surface waters and persist in the environment for extended periods of time.

The two fluorocarbons, 1,1,2-trichloro-1,2,2-trifluoroethane and trichlorofluoromethanes present a different type of hazard. Due to their high volatiliy, these two organics can rise into the stratosphere and deplete the ozone, leading to adverse health and environmental effects.

c. Damage incidents resulting from the mismanagement of waste solvents have been reported. These damage incidents are of three types:

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* The Agency is presently aware that these solvents may contain concentrations of additional toxic constituents listed in Appendix VIII of the regulations. For purposes of this listing, however, the Agency is only listing those wastes for the presence of the halogenated and non-halogenated solvents. The Agency expects to study these listings further to determine whether the waste solvent and still bottom listings should be amended.

(1) Fire/explosion damage resulting from ignition of the solvents;

(2) Contamination of wells in the vicinity of inadequate waste storage or disposal (with resulting illness in at least one instance); and

(3) Direct entry of solvent into a waterway, resulting in fish kills.

These damage incidents show that mismanagement occurs and that substantial hazard to human health and the environment may result.

C. Spent Waste Cyanide Solutions and Sludges

1. Quenching bath sludge from bath pot cleaning from metal heat treating operations (R, T) - 5/19/80

2. Spent solutions from salt bath pot cleaning from metal treating operations (R, T) - 5/19/80

3. Quenching wastewater treatment sludges from metal heat treating operations (T) 5/19/80

These wastes are considered hazardous based on the following:

a. Each of the wastes generated exhibits either reactive or toxic properties or both due to their cyanide content.

b. The land disposal of cyanide wastes containing high concentrations of cyanide is widespread throughout the United States.

c. Cyanides can migrate from the wastes to adversely affect human health and the environment by the following pathways, all of which have occured in actual management practices:

(1) generation of cyanide gas resulting from the reactive nature of cyanide salts when mixed with acid wastes;

(2) contamination of soil and surface waters in the vicinity of improper waste disposal resulting in destruction of livestock, wildlife, stream-dwelling organisms, and local vegetation; and

(3) contamination of private wells and community drinking water supplies in the vicinity of improper waste disposal.

These, then are the wastes, applicable to the steel industry, which have been specifically listed by EPA as being hazardous. This is not to say that these wastes are the only hazardous wastes generated by the steel industry. As was stated earlier, if the generator thinks or knows that he has other hazardous waste, he is required to report it to EPA for an identification number, performing testing, if necessary, to make the determination of hazardousness.

These wastes, due to their being classified as hazardous, are subject to the interim status provisions, as previously discussed.

Non-Hazardous Wastes

Most of the solid waste generated by the steel industry will probably be non-hazardous. Wastes such as blast furnace slag, BOF sludge, and blast furnace dust will likely fall into this category.

The types and quantities of non-hazardous wastes estimated to be generated by the industry were shown in Table 1. Over 50 million metric tons of non-hazardous waste are generated per year. After commercial sale and/or in plant recovery, about 19 million metric tons (approximately equals 40%) of non-hazardous waste remain to be disposed. The most common disposal practice is to dump or landfill these wastes. EPA promulgated criteria for classifying non-hazardous waste disposal sites on September 13, 1979. These regulations establish eight Federal criteria for determining whether a disposal site is a "sanitary landfill" or an "open dump". The criteria include certain restrictions on siting in floodplains, contamination of surface and ground water, land-spreading of wastes, and open burning. Protection of endangered species, protection against disease vectors and explosive gases, and bird hazards to aircraft are also addressed.

If a facility is determined to be an open dump, by virtue of failing any one of the eight criteria, it must either be closed or upgraded to the status of a sanitary landfill within five years.

RCRA recognizes that prime responsibility for environmentally sound disposal and resource recovery rests with state and local government. Each state will evaluate the individual disposal sites, establishing its own priorities for listing open dumps. The states are required to develop a plan to identify a general strategy for protecting public health and the environment from adverse effects associated with solid waste disposal, for encouraging resource recovery and conservation, and for providing adequate disposal capacity in the state. The Federal criteria are the minimum requirements to be used in determining compliance.

Thus, the requirements imposed by each of the states for steel industry waste disposal facilities will be the controlling factor in determining whether a facility will be permitted. An approved state program could be more stringent than the Federal criteria but cannot be less stringent. It would be wise to ascertain the specific requirements of the states in which your facilities are or will be located.

Section 7002 of RCRA provides for citizen suits against the operator of an open dump, which may be enforced in Federal district court. EPA does not specifically have the authority to take legal action against parties that may violate the open dumping prohibition.

Impact on Steel Industry

The steel industry must dispose of over 6 million metric tons of hazardous waste and over 50 million metric tons of non-hazardous waste per year.

Although the steel industry presently recycles/recovers a significant portion of their wastes, a large quantity of wastes still remains to be properly disposed of. Up to this time, many of the wastes have been improperly disposed. A concerted effort will be required by the steel industry to reverse this trend.

Much of the steel industry is located in areas where land for disposal is scarce and if available - quite costly. Proper management of the wastes will certainly dictate that the waste management facility be designed and operated in the most effective manner to meet both environmental and economic concerns.

In a preliminary final economic impact analysis of Subtitle C interim status hazardous waste regulations prepared in April of this year, the impact on the steel industry was determined.[3] Tables 3 and 4 below illustrate the estimated impact.

The estimated impact on the steel industry was made in light of a number of assumptions, some of which were:

1. The EIA was based on the 10 x drinking water standard (DWS) rather than the promulgated 100 x DWS.

2. Analysis was made requiring much stricter closure requirements for landfills and surface impoundments than the promulgated regs.

3. Underground injection was not addressed in the Analysis.

Table 3

INCREMENTAL COST TO THE STEEL INDUSTRY OF RCRA INTERIM STATUS STANDARDS

Cost of Waste Management at the Generator Plant

Capital ($ Million)	1st Year Expenses ($ Million)	Annual Operating ($ Million)	Cost of Off-Site Transportation ($ Million)
9.33	4.56	7.02	0.19

Total Annual Cost ($ Million)	1978 Value Added ($ Million)	Annual Cost as a Percent of Value Added (Percent)
11 02	46,000	0.02

Table 4

ECONOMIC IMPACT ON THE STEEL INDUSTRY

Number of Existing Plants in 1978	Plant Closures	Job Losses	U.S. Production Cutbacks
152	negligible	negligible	negligible

Price Increases	U.S. Demand Reduction	Balance of Payments Effects
negligible	negligible	negligible

With regard non-hazardous wastes, an assessment was made (as presented in the EIS of December 1979) on the cost to the steel industry to meet the "RCRA Section 4004 Criteria for Classification of Solid Waste Disposal Facilities and Practices."[4] A number of assumptions, including the following were made:

1. 50% of steel industry solid waste is disposed onsite, 50% off-site.

2. All non-hazardous steel industry wastes will be disposed in a manner which meets the criteria requirements.

3. Disposal facilities will not be relocated as a result of the criteria.

4. The groundwater and floodplain criteria will probably have the greatest impact on the industry.

It was estimated that the total current annual disposal cost for steel industry non-hazardous wastes is slightly over $50 million. The annual cost of complying with the criteria was estimated at approximately $36 million, a resultant increase of about 72% in disposal costs. Groundwater protection accounts for the major portion of these increased costs.

It must be remembered that a significant number of the states in which steel industry disposal facilities are located already have regulations comparable to the 4004 criteria.[5] This is an important point since implementation and enforcement of the disposal criteria is the responsibility of the individual states. In fact, probably 80% of the estimated expected $36 million increase for non-hazardous waste disposal can be attributed to comparable State regulations. The remaining 20% of the increased costs can be assumed as being induced by the Federal 4004 criteria.

The overshadowing goal of RCRA is resource recovery and conservation. I am sure that all of you know that the United States recovers far less of its industrial wastes than many other industrialized nations. One of the major contributing factors to these low recovery statistics is the availability of cheap disposal options. Proper disposal will inevitably raise the cost of disposal, thus increasing the viability of recovering incremental amounts of waste materials. The steel industry is to be applauded on its already high rate of (60-70%) waste recycling. However, much remains to be done in this respect. Significant quantities of solid waste that are presently disposed of could be recycled, thereby not only preventing the wasting of valuable natural resources but also extending the life of landfills by decreasing the quantity of waste to be disposed and eliminating potential contamination threats to our nations surface and ground waters.

EPA firmly believes that resource recovery should be implemented whenever possible as an alternative to land disposal of solid wastes. We wholeheartedly support and encourage studies regarding the potential recovery/recycle of steel industry wastes.

Examples of two such studies currently underway by EPA's Office of Research and Development (ORD) are:

1. "Investigation of Toxic Substances during Recovery and Recycle of Steel Industry Iron Bearing Solid Waste"; and
2. "Uses for Ferrous Sulfate Heptahydrate from Steelmaking Spent Pickle Liquor".

These studies will be discussed in detail this morning. Although the Office of Solid Waste is not presently sponsoring any studies of the steel industry, we will be evaluating the work of others and may issue industry specific waste recovery and disposal guidelines in the future.

In this era of environmental concerns and economic struggles, it is hoped that industry and government will develop a cooperative working relationship towards solving the problems faced by the steel industry.

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SPENT SULFURIC PICKLE LIQUOR RECOVERY
ALTERNATIVES AND BY-PRODUCT USES

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Each year, sulfuric acid pickling of steel produces approximately 600 million gallons of spent sulfuric pickle liquor (SSPL). Currently, contract hauling is the most prevalent SSPL disposal method. Only a small portion of the SSPL is processed for sulfuric acid recovery. Resource recovery and environmental protection objectives favor recovery instead of disposal. Commercial recovery processes involve separation of iron salts resulting in a relatively pure ferrous sulfate by-product. This paper summarizes a recent study of alternate SSPL recovery technologies, the identification of valid end uses for the ferrous sulfate by-product, and process economics.

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SPENT SULFURIC PICKLE LIQUOR RECOVERY ALTERNATIVES AND BY-PRODUCT USES

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INTRODUCTION

Before steel products can be given a final surface coating or finish, the surface must be cleaned of any scale and rust that may have formed due to exposure to the atmosphere. The process most commonly used in removing surface scale and rust from iron and steel products is acid pickling. The removal is accomplished by immersing the scaled steel in tanks of hot dilute acid, such as hydrochloric or sulfuric acid. As the scale dissolves in the acid, iron salts are formed and the pickling solution becomes ineffective. Recovery or disposal of the waste pickle liquor poses a potential environmental problem.

Of the estimated 91 million tonnes (100 million tons) of steel shipped in 1979, approximately 22 million tonnes (25 million tons) were pickled by sulfuric acid. This pickling operation produced an estimated 2.3 billion liters (600 million gallons) of spent sulfuric acid pickle liquor. Currently, the acid is either recovered or disposed of by contract hauling, deep-well injection, neutralization/ponding, discharge to a waterway or discharge to a publicly-owned water treatment facility. Spent pickle liquor is also in limited direct use as a water treatment chemical. Of all these methods, acid recovery is very favorable based on resource recovery and environmental protection objectives.

Acid recovery processes involve the removal of iron as ferrous salt crystals to regenerate the acid solution. Recovered sulfuric acid can be returned to the pickling process as a somewhat dilute makeup. The water-soluble ferrous salt by-product can either be sold for its chemical value or disposed of in a secured landfill. Although sale of the by-product is definitely the preferential course of action, it depends primarily upon the market demand for this material including the manufacture of products such as colored pigments and magnetic tapes. Furthermore, since acid recovery is not widely used at this time, implementation of this process by a majority of the steel industry could produce an oversupply of the by-product. Therefore, before acid recovery can be encouraged as an environmentally acceptable method of handling spent sulfuric acid pickle liquor, adequate by-product end use markets must be identified and evaluated.

The objectives of this program were to evaluate the commercially available processes for recovering spent sulfuric acid pickle liquor, estimate the quantity and quality of by-product generated by these processes, and identify the current and potential end use markets for such by-products. Information for this study was obtained by thoroughly reviewing the available technical literature, visiting steel mills with operating acid recovery processes, meeting with representatives of the steel industry, and contacting process vendors, by-product end users, and other knowledgeable steel industry personnel.

SULFURIC ACID PICKLING

Sulfuric acid pickling of steel can be either a batch or continuous operation. In the case of wire or rod, the steel is suspended from overhead conveying racks and dipped into a single vat of pickle liquor for a designated period of time. For rolled sheet steel, the metal is continuously passed through a series of acid vats, each successive tank containing a slightly more acidic pickle liquor.

In sulfuric acid pickling, the scale is not only removed by acid dissolution but also by the effervescent action of hydrogen gas formation under the scale. The sulfuric acid reacts with the iron base on the surface of the steel to produce hydrogen gas and ferrous sulfate according to the following reaction:

$$Fe + H_2SO_4 \rightarrow H_2\uparrow + FeSO_4$$

The scale which is removed from the surface then slowly dissolves in the pickling tank to produce additional ferrous sulfate as shown in the following reaction:

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$$

Increasing amounts of ferrous sulfate from continued use eventually consume enough sulfuric acid to render the liquor ineffective for further pickling.

Besides the presence of acid in the pickling tank, other chemicals may be added to improve the quality of the pickled product. Various organic inhibitors are frequently used in pickling to inhibit acid attack on the base metal, while permitting preferential attack on the scale. In addition, wetting agents may be used to improve the effective contact of the acid solution with the metal surface.

After pickling, the steel product is rinsed with water to remove any adhering acid. In some cases, the pickled product may then be coated with lime, oil or some other material to protect it from exposure to the atmosphere.

A recent EPA survey estimates that in 1979 sulfuric acid pickling accounted for about 42.9% of all the steel products pickled in the United States.[1] Pickling with hydrochloric acid and mixed acids accounted for the remaining 45.8% and 11.3%, respectively. According to this same survey, approximately 105 of 133 major steel picklers use sulfuric acid in batch systems while 44 use sulfuric acid in continuous systems. Hydrochloric acid is used by 6 plants in batch systems and 41 plants in continuous systems.[1]

In the 1960's, the trend in pickling was to switch from sulfuric acid to hydrochloric acid. This conversion occurred for several reasons. At the time, hydrochloric acid was readily available and relatively inexpensive. In addition, pickling with HCl is somewhat faster than using sulfuric acid and the pickling solution retains its effectiveness longer. Furthermore, hydrochloric acid is considered to give a "brighter" finish. Recently, however, the conversion from sulfuric acid to hydrochloric acid has apparently ended for two reasons. First, the price of hydrochloric acid has increased such that it is no longer economically attractive. And second, fumes generated during HCl pickling are a difficult and expensive air pollution control problem. Therefore, the percentage of steel products being pickled by sulfuric acid will probably remain the same in the near term.

PICKLING WASTES

Waste pickle liquor is generated when the pickling solution becomes saturated with iron salts. The pickle liquor is no longer effective in removing scale and, consequently, must be replaced. In addition to free sulfuric acid and iron salts (typically 8.0 wt % each), the spent pickle liquor may contain varying amounts of lubricants, suspended solids, heavy metals, and additives such as inhibitors. Table 1 presents the overall range of compositions determined from the analyses of several waste pickle liquor samples.[1] Since a variety of chemical additives may be used in pickling operations, the quantity and composition of these additives in waste pickle liquor is not reflected in Table 1. However, the presence of these additives is also of environmental concern in the handling of waste pickle liquor.

Table 1. Analyses of sulfuric acid pickling wastes (mg/l)[1,2,3]

Parameter	Spent Pickle Liquor	Rinse Water	Scrubber Blowdown
Dissolved Iron	38,750-66,500	36-2900	≤305
Oil and Grease	8-35	≤22	2-30
Suspended Solids	236-2363	≤750	2-200
Arsenic	≤0.1	≤0.33	
Cadmium	≤0.6	≤0.13	
Chromium	6-269	≤3.8	
Copper	≤4.7	≤10.4	
Cyanide	ND	≤0.1	
Lead	≤10	≤2.0	
Nickel	6.8-27	≤4.6	
Silver	0.28-0.59	≤0.85	
Zinc	0.7-244	≤59	

ND - indicates that the component was not detected.

The amount of spent pickle liquor generated will depend on the original quality of the pickle liquor and the amount of surface scale on the steel product. Based on a 1.0% iron loss, pickling 0.9 tonnes (1.0 ton) of steel will generate 95 liters (25 gallons) of spent pickle liquor. Assuming 22 million tonnes (25 million tons) of steel were pickled by sulfuric acid in 1979, then the resulting volume of waste pickle liquor was approximately 2.3 billion liters (600 million gallons) containing 220,000 tonnes (250,000 tons) each of free acid and dissolved iron.[3] These values illustrate the significant potential for sulfuric acid recovery and by-product manufacture.

In addition to spent pickle liquor, steel pickling processes may generate two other wastewater streams: acidified rinse water and scrubber blowdown. Acidified rinse water results from washing the pickled product to remove any adhering pickle liquor. Methods of rinsing may vary from a single-stage immersion to a multi-stage system. Many steel companies are switching from rinse systems that flush the steel with large quantities of water to systems that use fine sprays. Depending on the overall water balance for the pickling operation, rinse water can frequently be used as makeup for the pickling tanks. Table 1 presents the overall range of compositions determined from the analyses of several rinse water samples.

Scrubber blowdown results from emission control equipment to collect and absorb acid fumes and mists emitted from the pickling tanks. A wet scrubber typically recylces water with a small purge or blowdown stream to control the levels of sulfuric acid. Under efficient operation, the scrubber may achieve less than 3% blowdown, which can be used as makeup to either the rinse system or the pickling tanks. Table 1 presents the overall range of compositions determined from the analyses of several scrubber blowdown samples.

WASTE PICKLE LIQUOR DISPOSAL TECHNIQUES

Currently, waste pickle liquor disposal includes

- contract hauling,
- deep-well injection,
- neutralization/ponding,
- discharge to a waterway,
- discharge to a publicly-owned water treatment facility,
- direct use as a water treatment chemical, and
- acid recovery.

The three most commonly used disposal techniques are contract hauling, deep-well injection, and neutralization.

Contract hauling has long been a favorable means of handling waste pickle liquor because of moderate operating cost and little or no capital cost to the steel industry. However, the growing cost of energy for transportation is being reflected by an increased operating cost for disposal by contract hauling. Furthermore, the operating cost for contract hauling can be expected to increase even more as regulatory agencies enact stricter controls on disposal. From 1970 to 1980, the cost of contract hauling has risen approximately 340%, from 0.9¢/liter (3.5¢/gallon) to 3.2¢/liter (12¢/gallon).[4,5]

A second popular method of waste pickle liquor disposal is deep-well injection. However, this disposal method is limited to favorable subsurface geological formations that will protect local groundwater from contamination. Current estimates indicate that only a dozen or so wells in the U.S. are used for the disposal of waste pickle liquor, with a majority of these wells being located in North Central Illinois and Northwestern Indiana.[6,7] Although deep-well injection has been used for many years, concern over the potential for groundwater contamination may mean stricter regulatory control and possibly an end to this method of disposal.

Neutralization of waste pickle liquor with lime, soda ash or caustic soda has been an established practice for some time. Addition of these chemicals increases the initially acidic pH of the pickle liquor to a neutral level. The increasing pH causes the iron to precipitate as a gelatinous iron hydroxide sludge which settles very slowly. Hence, the neutralized mixture is placed in a pond where it can be contained indefinitely. The cost of waste pickle liquor disposal by neutralization/ponding has been steadily increasing over the past several years. The increasing cost primarily reflects the rapidly rising cost of chemicals, particularly lime, and the inherent value of the land required for lagooning.

Each of the three previously described disposal methods for waste pickle liquor are currently in widespread use. None of these disposal techniques makes any attempt to recover the acid or dissolved iron. In some instances, these methods may be trading one type of environmental problem for another. On the other hand, the use of acid recovery units results in the recovery of sulfuric acid and an iron salt by-product, and virtually eliminates water pollution associated with sulfuric acid pickling operations.

ACID RECOVERY PROCESSES

Two types of acid recovery processes are commercially available: high temperature and low temperature. High temperature processes heat the waste pickle liquor to about 93°C (200°F) and produce a ferrous sulfate monohydrate (FSM) precipitate. These processes are not widely used because of the associated high energy costs and the problems of ferrous sulfate monohydrate scaling. At present, two such acid recovery processes are in operation in the U.S.: A Pureco unit at Wilson Steel and Wire in Chicago and a Sulfex unit at Metal Processing Company in Maple Heights, Ohio.

Low temperature acid recovery processes cool the waste pickle liquor to about 15°C (45°F) and produce a ferrous sulfate heptahydrate (FSH) precipitate. Commercially, three low temperature processes are available in the U.S.: the Kerachemie, the Crown, and the KSF processes. The Crown and KSF processes are the most widely accepted of the low temperature acid recovery processes. One Kerachemie unit has been installed in the United States (Fitzsimmons Steel Company, Youngstown, Ohio), but it is no longer in use at the plant.

Both the Crown and the KSF acid recovery processes are modular batch-type units. Each unit consists of a chiller/crystallizer, a slurry separator, and separate storage for recovered acid and by-product crystals. Waste pickle liquor is fed to the crystallizer and cooled by submerged chilling coils. The Crown process lowers the temperature of the waste pickle liquor to about 2-10°C (35-50°F) by circulating freon refrigerant through Teflon cooling coils. The KSF process uses chilled water to achieve a temperature of about 7-10°C (45-50°F). As the temperature of the waste pickle liquor decreases, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) crystals begin to form. In both processes, a motor-driven agitator stirs the acid/crystal slurry to maintain a uniform temperature and to prevent the crystals from agglomerating into large chunks.

The slurry is pumped from the chiller/crystallizer to a separation unit for removal of the ferrous sulfate heptahydrate crystals. The recovered acid can either be recycled to the chiller for additional processing or stored for future acid makeup to the pickling operations. The by-product FSH crystals can be washed to remove any sulfuric acid adhering to the surface. The wash water is recycled to the chiller for additional processing. As indicated by Table 2, the by-product crystals are relatively pure ferrous sulfate heptahydrate and can be sold as a source of iron for several uses.[5] Since the FSH crystals are water-soluble, its storage should be protected from the weather.

Table 2. Analysis* of ferrous sulfate heptahydrate by-product (wt. %).[5,8]

	Crown System	KSF System
$FeSO_4 \cdot 7H_2O$	99.4	99.98
Sulfate	0.39	
Free acid (H_2SO_4)		<0.03
Iron (Fe^{++})	0.20	
Copper	0.0025	0.0001
Lead	0.0050	0.0003
Manganese	0.01	0.01
Zinc	0.0010	0.0002
Calcium	0.0017	0.0002
Sodium	0.0160	<0.0001

*Method of analysis - atomic absorption.

Economically, acid recovery compares very favorably with neutralization and contract hauling as a means of handling waste pickle liquor. Table 3, from an EPA report, illustrates an economic comparison of these waste pickle liquor alternatives.[4] Although sale of the by-product FSH crystals is certainly an advantage to recovering acid, the credit for by-product sale is not the most critical factor in making acid recovery economically attractive. Other major cost advantages for using acid recovery include a credit for process water reuse, negligible wastewater requirements, a credit for recovered acid reuse, and reduced transportation costs. The major economic disadvantages of acid recovery systems are capital investment and utility requirements.

The economic disadvantage of capital investment could be diminished by using regional acid recovery facilities to handle the waste pickle liquor treatment needs for several plants in a local area. Such a facility could be owned and operated either jointly by many steel picklers or independently by an outside individual or company. The joint ownership option has been in operation in West Germany for several years. Although this method of ownership reduces the amount of capital any one company must invest in an acid recovery system, the approach also has disadvantages.

Table 3. Economic comparison of waste pickle liquor treatment alternatives.[4]
(Total Annual Costs, $1,000)

Item	Acid Recovery	Neutralization	Contract Hauling
Investment	630.0	770.0	0
Salaries & Wages			
Operators	12.5	12.5	6.2
Foremen	1.5	3.8	0
Utilities			
Steam	35.4	4.2	-
Process Water	(8.1)	-	-
Electricity	19.0	4.0	-
Raw Materials			
H_2SO_4	(50.0)	-	-
CaO	0	68.7	0
Shipping & Hauling Costs			
Crystals	28.8	0	0
Sludge	0	110.0	0
Pickle Liquor	0	0	350.0
Maintenance	37.8	46.2	-
General Plant Overhead	36.0	41.7	7.8
Wastewater Costs			
Sewer Fees	0	9.2	10.0
pH Adjustment	0	0	62.5
Taxes and Insurance	3.2	3.9	0
Depreciation	63.0	77.0	0
FSH By-Product Credit	(52.0)	0	0
Total Annual Costs	126.1	381.2	436.5

Rinse Water included in process water for acid recovery plants at 25 gal/ton pickled steel.

Basis: 100,000 tons/yrof steel pickled; 1% iron loss; spent pickle liquor composition 8% dissolved iron, 8% H_2SO_4 all figures in thousands of dollars per year (1976 base).

One of the major disadvantages associated with regional acid recovery systems is transportation of the waste pickle liquor to the facility. Currently, waste pickle liquor is classified as a hazardous material. Therefore, its transport may be highly limited or even restricted in certain areas and would be subject to RCRA regulations with attendant costs. Also, the rising cost of fuel means that transporting large quantities of waste pickle could become fairly expensive. This factor is already being reflected in the increasing cost of contract hauling. Transportation and storage of waste pickle liquor could be further complicated by premature precipitation of ferrous sulfate heptahydrate under cold climatic conditions. Heated or insulated vehicles and storage vessels would eliminate this potential problem, but would also increase associated costs.

Another problem that may be encountered with regional facilities is the need to segregate waste pickle liquor by source. Since many steel picklers use proprietary additives in the pickling operations, the waste pickle liquor from each plant will require separate processing. The use of such additives makes it essential that a plant receive acid recovered from its own pickle liquor because some additives may cause adverse effects in a different pickling operation. Therefore, adequate pickle liquor and recovered acid storage governed by a strict accounting procedure tracking source and final destination will be required. In order to maintain flexibility for dumping ineffective batches, it will also be necessary for steel picklers to have on-site storage for waste pickle liquor and makeup acid.

Individually, none of these difficulties is insurmountable; collectively the disadvantages of relying on a regional acid recovery facility appear to overshadow the advantage of reduced capital cost to the pickling plants.

BY-PRODUCT MARKET

Although the economics of acid recovery is not strongly dependent on the sale of by-product ferrous sulfate heptahydrate (FSH), proper use of the water-soluble crystals is essential for acid recovery to be considered an environmentally acceptable method of handling waste pickle liquor. Therefore, a major focus of this study was to investigate the sources of FSH production and to identify and evaluate current and potential end use markets for FSH.

Comprehensive data for annual production, consumption, and prices for FSH are not available. However, rough estimates can be made using information from various sources. The current annual U.S. capacity for FSH production is about 363,000 tonnes (407,000 tons). Of this amount, approximately 296,000 tonnes (332,000 tons) is manufactured by eight chemical companies which act as commercial producers for the U.S. market.[9] Yet, as much as 98,000 tonnes (110,000 tons) of this capacity may soon be removed from service for various reasons.[10] At present, acid recovery processes for pickling operations have the capacity to produce 67,000 tonnes (75,000 tons) of FSH, which represents only 18% of the total U.S. capacity.[11] In addition to current domestic FSH production capacity, an estimated 93,000 tonnes (104,000 tons) is imported from West Germany, Japan and Mexico.[10] These figures indicate that the U.S. market for FSH is strong enough for imports to absorb the cost of transportation and still be sold at a profit.

The market price for ferrous sulfate heptahydrate can vary considerably. The current market price for moist (having some surface water) FSH is about \$19 per tonne (\$17 per ton).[10] However, in the Midwest, the market price for moist FSH by-product from acid recovery processes ranges from \$2 to \$50 per tonne (\$2 to \$45 per ton).[12] Imports from West Germany are usually transported up the Mississippi River by barge and marketed in the Midwest for approximately \$34 per tonne (\$30 per ton).[10] Dry ferrous sulfate heptahydrate has had the surface moisture removed by a moderate heating process and currently sells for \$101 per tonne (\$90 per ton).[10] Ferrous sulfate heptahydrate can also be converted to the monohydrate form by heating. Ferrous sulfate monohydrate currently sells for \$190 to \$224 per tonne (\$170 to \$200 per ton).[10]

At present, FSH is used almost exclusively as a source of synthetic iron oxide for the manufacture of pigments, ferrites and magnetic tapes, fertilizers and animal feed, and catalysts and for water and sewage treatment. As Table 4 indicates, the two major end uses are colored pigments and magnetic tapes, accounting for 45% and 35%, respectively, of the total FSH consumption in 1978.[13,14]

Table 4. Ferrous sulfate consumption by end use, 1978 and 1972.[13,14]

	1978	1972
Iron oxide pigments	45%	45%
Magnetic tapes and ferrites	35%	30%
Fertilizers and stockfeed	8%	12%
Water and sewage treatment	5%	5%
Catalysts	3%	3%
Miscellaneous	4%	5%
Total	100%	100%

In recent years the pigment industry has been a large consumer of ferrous sulfate heptahydrate as a source of iron oxides. In 1974, 121,000 tonnes (135,000 tons) of iron oxides were consumed in the production of colored pigments.[15] Of this amount, slightly more than half (53.3%) was supplied by synthetic (by-product) oxides as opposed to natural oxides derived from pulverized iron ore and pyrite cinders. Although the cost of synthetic oxides is approximately three to four times greater than natural oxides, the synthetic oxides are preferred because they provide a wider range of colors and brillance. Furthermore, synthetic oxides function well in water-based paints and many natural oxides do not. This factor is important in that a growing trend to water-based paints as a means of reducing atmospheric solvent emissions will probably mean an increased demand for synthetic iron oxides.

The use of ferrous sulfate heptahydrate as a source of iron oxides for magnetic tape manufacturing has been steadily increasing. Currently, only a few companies produce synthetic iron oxide for magnetic recording. Yet, the future demand for ferrous sulfate as a raw material in magnetic tape manufacturing should be strong. This prediction is based on the fact that the demand for magnetic tapes is closely associated with the high technology electronics industry, which has been experiencing consistently rapid growth during the last two decades. Similarly, the demand for hard and soft ferrites in electronics should parallel the growth of the industry. Iron oxides recovered from the by-products of waste pickle liquor processing have been used as a raw material in producing hard ferrites which are used in permanent magnets.[15]

Although water and sewage treatment have typically only accounted for 5% of the annual FSH consumption, this particular market represents the greatest area of potential use in the near future. Ferrous sulfate heptahydrate is used as a coagulant in the treatment of drinking water, as an additive for sludge fixation, and as an agent for phosphorus removal in municipal wastewater treatment. The key potential use for FSH is as an agent for phosphorus removal.

Phosphorus control is considered critical in some bays, coastal areas, and drainage basins of lakes. It is especially critical in the drainage basins of the North American Great Lakes, which contain approximately 20% of the world's supply of surface fresh water. The International Joint Commission (IJC) of Canada and the United States established a program in 1978 to minimize eutrophication problems in the Great Lakes by reducing phosphorus inputs. Consequently, increasing demand for chemicals used in phosphorus removal can be expected in the eight states along the Great Lakes. Six of these states are also among the top ten steel producing states. Hence, pickling plants in this area which use acid recovery could possibly have a fairly substantial local market for the by-product ferrous sulfate heptahydrate.

Currently, several chemicals are being used to remove phosphorus from municipal wastewater, including aluminum sulfate (alum), sodium aluminate, ferric chloride, ferrous chloride, ferric sulfate, and lime. Of all these chemicals, alum and ferric chloride are the most widely used. In the lower Great Lakes basins, iron salts and aluminum salts equally share about 99% of the chemical market for phosphorus control.[16] Data concerning the types of iron salts (e.g., ferric chloride, ferrous chloride, ferrous sulfate) used are not available.

Although alum and ferric chloride are widely available and well known to wastewater treatment plant designers and operators, ferrous sulfate can compete both technically and economically with both of these chemicals. Technically, ferrous sulfate can reduce effluent phosphorus as effectively as commonly used chemicals. Based on FSH chemical analyses (Table 2) introduction of other pollutants should be no more of a problem than with other chemicals. Other concerns, such as pH changes and metal leakage, are common to most phosphorus precipitating chemicals and will depend in some measure on the proper operation of the treatment facility. Furthermore, storage, feed and treatment equipment should not vary significantly for different chemicals, so that minimum modifications will be required to switch from alum or ferric chloride to ferrous sulfate.

Economically, ferrous sulfate is a very attractive alternative to alum and ferric chloride. Since utilities (electricity), operator time and other operating costs are typically low relative to raw material costs, the economics of phosphorus removal is basically governed by the cost of the treatment chemical. Table 5 presents an economic comparison of phosphorus removal by different chemicals (exclusive of transportation costs). This comparison indicates that use of ferrous sulfate heptahydrate has a reasonable economic advantage over the use of ferric chloride and a significant economic advantage over the use of alum. However, transportation may add significantly to the cost of chemicals, and thus the shipping distance may be the primary factor in chemical selection. For states bordering the Great Lakes, transportation costs for ferrous sulfate heptahydrate from acid recovery processes should be minimal due to the proximity of the pickling operations.

Table 5. Economic comparison of phosphorus removal by different chemicals.

Chemical	Requirement per Unit of Phosphorus Removed		Chemical Cost	Phosphorus Removal Cost
	kg/kg or lb/lb	liter/kg (gal/lb)	\$/tonne (\$/ton)	\$/kg (\$/lb)
Alum - $Al_2(SO_4)_3 \cdot 14.3H_2O$				
Dry - 9 wt % Al ion	22.2		119 (120)	2.93 (1.33)
Liquid - 4.4 wt % Al ion		34.2 (4.1)	100 (110)	5.51 (2.50)
Sodium Aluminate - $Na_2Al_2O_4$				
Dry - 45 wt % Al_2O_3	8.4		816 (900)	8.33 (3.78)
Liquid - 26 wt % Al_2O_3		10.0 (1.2)	272 (300)	4.96 (2.25)
Ferric Chloride - $FeCl_3$				
Liquid - 40 wt % $FeCl_3$		10.0 (1.2)	96 (106)	1.68 (0.76)
Ferric Sulfate - $Fe_2(SO_4)_3 \cdot 7H_2O$				
Dry - 19.5 wt % Fe^{3+}	10.3		106 (117)	1.32 (0.60)
Ferrous Sulfate Heptahydrate - $FeSO_4 \cdot 7H_2O$				
Dry - 20 wt % Fe^{2+}	10.0		68 (75)	0.84 (0.38)

Basis:
1) Metal ion to phosphorus removed weight ratio of 2.0 to 1.0 for all metal ions
2) 10.0 mg/l phosphorus inlet concentration
3) <1.0 mg/l phosphorus effluent concentration
4) Phosphorus removal with secondary treatment

Estimating the potential market for FSH by-product in the municipal wastewater treatment sector is difficult. Based on a wastewater flow of 380 liters (100 gallons) per capita per day and a phosphorus removal of 9.5 mg/l, then the potential market for ferrous sulfate heptahydrate in the Great Lakes States is estimated to be 1.0 million tonnes (1.12 million tons) in 1985. If all U.S. sulfuric acid pickling operations practiced acid recovery in 1985, the estimated FSH by-product generated would be almost 740,000 tonnes (830,000 tons). Therefore, the FSH by-product generated by all acid recovery sulfuric acid pickling operations in the U.S. (ignoring other FSH end use demands) would only be able to supply 73.2% of the total demand for municipal wastewater treatment in the Great Lakes area. If ferrous sulfate heptahydrate replaced alum and ferric chloride as the most popular chemical agent for controlling phosphorus in wastewater effluent, the demand for FSH could easily exceed the supply.

CONCLUSIONS

Acid recovery is economically competitive with contract hauling and neutralization. A major portion of the overall annual cost for acid recovery is due to capital investment. Using regional acid recovery facilities to treat waste pickle liquor from several local plants is a potential means of reducing the capital investment for any of the participating plants. However, these regional facilities do not appear practical for three reasons. First, transportation costs will be excessive because of the large volumes involved and the potential for premature iron salt precipitation. Second, processing costs will be increased by the need to segregate waste pickle liquor and recovered acid by company in order to prevent recovered acid contamination from different proprietary chemical additives. Finally, the cost to each steel mill is increased by the need to have waste pickle liquor and recovered acid storage facilities on-site in order to maintain flexibility with regard to spent acid dumping.

The demand for by-product FSH as a raw material for the production of iron oxide pigment could increase more dramatically than historically indicated. The cause of this sudden potential increase is two-fold. First, almost 30% of the current U.S. FSH production capacity will be removed from service for various reasons in the near future. Second, the need to reduce fugitive emissions from painting operations will mean an increase in the use of water-based paints which require pigments produced from synthetic sources such as by-product FSH. Combined, these two factors indicate a much stronger demand for by-product FSH in future iron oxide pigment production.

The potential impact of the municipal wastewater treatment market as an end use for FSH is difficult to assess. Rough estimates indicate this potential to be much greater than any of the current demands for FSH. For instance, if all U.S. sulfuric acid pickling operations practiced acid recovery in 1985, the estimated amount of by-product FSH generated would be 740,000 tonnes (828,000 tons). If all eight of the Great Lake states used strictly FSH instead of alum or ferric chloride for phosphate removal, the total estimated FSH required in 1985 would be almost 1,000,000 tonnes (1,130,000 tons). Therefore, FSH from acid recovery would only be able to supply 73.2% of the total demand for municipal wastewater treatment in that area alone. Clearly, the potential market for by-product FSH from waste pickle liquor recovery is considerable.

RECOMMENDATIONS

Although acid recovery represents the only method of recovering and reusing the chemical constituents found in waste pickle liquor, only 10% of the total spent sulfuric acid pickle liquor generated each year is treated by acid recovery. Since pickle liquor recovery is currently not a widespread practice, additional studies should be undertaken to evaluate the influence of spent pickle liquor composition on the quality of FSH by-product and recovered acid. Experience to date indicates that product quality has not usually been a problem. However, each pickling operation is a unique case and it may be that under certain conditions, recovered acid may be unsuitable for reuse, and/or FSH by-product may be unsuitable for sale. Therefore, better correlation of data pertaining to pickle liquor composition, recovery process operation, and acid and by-product quality is needed.

The reuse of by-product FSH is a major factor in assessing the environmental advantages of using acid recovery. Currently, the demand for FSH exceeds supply. Widespread use of acid recovery by sulfuric acid picklers could reverse this situation. However, the use of FSH as a chemical agent for controlling phosphorus levels in municipal wastewater appears to be a largely untapped market. Although limited use of FSH in wastewater treatment indicates very satisfactory removal of phosphorus, use at other wastewater treatment plants will probably involve evaluation on a case-by-case basis to assess the true removal effectiveness under a number of different conditions. This is an important factor in determining if FSH can displace alum and ferric chloride as the primary chemical for phosphorus control. Such an investigation might begin with a comparison of data from previous applications under similar conditions and continue with bench-scale laboratory studies or on-site pilot plant testing.

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ENVIRONMENTAL APPRAISAL OF RECLAMATION PROCESSES FOR STEEL INDUSTRY, IRON-BEARING SOLID WASTE

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ABSTRACT

The objective of this study was to investigate existing and emerging processes for the reclamation of the three largest quantities of iron-bearing solid wastes being landfilled by the steel industry--oily mill scale, steelmaking dust, and blast furnace dust and sludge. The processes considered are designed to remove contaminants to the degree that resource recovery (recycle) can be practiced. This paper summarizes the results of this study in terms of process identification and description, appraisal of the environmental aspects of reclamation including the appraisal of the potential for new environmental problems, and considers the economics and energy requirements of the various processes.

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In September of 1980, the Steel Tripartite Committee(1) report was released on Technological Research and Development in the Steel Industry. Pertinent to this study are a recommendation and a statement in the Tripartite report. The recommendation was that "government support should be given to the development of technologies and plant practices for recycling hazardous wastes produced in steel manufacturing". The statement was that "environmental and occupational safety and health issues should be considered as an integral part of technological research and development in the steel industry..."

This paper deals with an environmental appraisal of reclamation processes for steel industry, iron-bearing solid waste. This appraisal study was funded by the EPA's Industrial Environmental Research Laboratory (IERL-RTP) and as an appraisal it is in line with both stated sentiments of the R & D Group of the Tripartite Committee.

TECHNICAL OBJECTIVE AND SCOPE OF THE STUDY

The overall objective of this study was to investigate existing and emerging processes for the reclamation of steel industry iron-bearing wastes being landfilled. These reclamation processes should be capable of extracting and/or eliminating undesirable contaminants to the degree that the processed material is acceptable for recycle. If this were possible in operations that did not introduce new pollution problems, it would result in a conservation of resources and a decrease in problems pertaining to waste management. The term "investigate" in this instance included:

(1) Identification and description of processes including capability and mass and energy balances, where available

(2) Appraisal of the potential for new environmental problems that may be part of these existing and emerging processes

(3) Appraisal of the overall economics of reclaiming and/or using approved landfilling for contaminated solid wastes

(4) General ranking of the processes including identification of any remaining environmental problems.

Definitions and Listing of the Types of Wastes of Interest in This Study

The U.S. steel industry routinely recycles about 80 percent of its solid wastes.(2) The remaining 20 percent is not recycled because the material is either (a) nearly worthless, e.g., trash, rubble, and some slags, or (b) although valuable, the material is contaminated with troublesome elements from either an operational or product viewpoint.

One viewpoint of metallurgical processing is that it is the science/art of separating (by many routes) the desired element(s) from the undesirable elements or compounds that are almost always present in the starting materials, i.e., the undesirable elements in ores, coal, scrap, etc. It is self-evident that there must be an "outlet" for the contaminating materials from an operational viewpoint. In the past, this "outlet", generally speaking, was either simple landfilling (dumping) or storage, i.e., landfilling awaiting a suitable, profitable reclamation process.

In this report, a reclamation process is defined as a method of rescuing a material from an undesirable state. For contaminated materials, an ideal reclamation would economically separate for use both the contaminant(s) and the purified basic material for recycle (e.g. to obtain oil and oil-free mill scale from oily mill scale).

This study is focused on reclamation processes for steel industry, iron-bearing wastes (now being dumped) which offer the best potential for the greatest recovery of iron and possible valuable by-products (former contaminants). Included is iron-bearing electric-arc furnace steelmaking dust that are now listed as being hazardous (leachable) when placed in ordinary landfills.(3) The waste materials of interest in this study are listed in Table 1.

Introduction to the Reclamation Processes Appraised in This Study

This paper presents information and appraisals on four specific reclamation processes and one general type of a pyrometallurgical reclamation process that has many variations. The format for presenting information is according to the iron-bearing waste name or type. Two processes, one used at Inmetco of Ellwood City, Pennsylvania and the other at Huron Valley Steel of Toledo, Ohio, were not included because they were learned of too late for inclusion in this study.

A process is regarded as "existing" if it is, or has been, in operation on a plant scale. The designation of "an emerging process" is more arbitrary. If a process has reached the pilot plant stage or has been tested even briefly on a pilot or plant scale, and there are technical reasons for believing that the desired technical results can be achieved, it was considered an emerging process.

Almost all of the individual processes are the development of a single organization or company. For proprietary processes the commercial interests of the owners often limited the amount of information that was released.

RECLAMATION PROCESSES FOR THE DEOILING OF MILL SCALE

Scale is the oxidized surface layer that forms on semi-finished steel during the heating and hot-working operations in rolling mills. During the hot-forming operations (multiple steps) the mill scale is periodically broken away from the steel shape by breaker rolls and/or water and steam jets.

TABLE 1. STEEL INDUSTRY, IRON-BEARING SOLID WASTES(2) OF INTEREST IN THIS STUDY

Waste	Amounts of Waste Landfilled per 125 Million Tonnes of Steel Produced (millions of tonnes)	Range of Iron Content, percent	Reasons For Landfilling
Mill Scale (67% of total is recycled)	1.7	58 to 70	Oil content too high for trouble-free recycling via sintering
Steelmaking Dusts and Sludge* (20% of total is recycled)	1.8	45 to 60	Zinc and/or alkali content too high for recycling to blast furnace
Blast Furnace Dust and Sludges** (78% is recycled)	0.75	10 to 40	Contaminated with oil and non-ferrous compounds

* - This represents the amount of landfilled dust and sludges from the pollution control equipment on all U.S. steelmaking processes. The total dust from electric-arc furnace steelmaking is about 350,000 tonnes or about 20 percent of the total weight of steelmaking dust collected. Electric-arc furnace dust is listed as hazardous because of the leachable lead, cadmium, and chromium content.

** - This represents the 22 percent of the total dust and sludge collected at blast furnaces which is not recycled.

As the scale is broken away from the hot steel it falls through the roll tables into a water flume. Also entering the flume are variable quantities of lubricating greases and oils from the rolling machinery. In the carryout of scale, it passes a series of traps or basins which provide an automatic size classification system. The large particles with a low oil content are collected at the beginning of the system; on the other end of the system, there is an oil sludge in the clarifiers which has a small amount of mill scale fines.

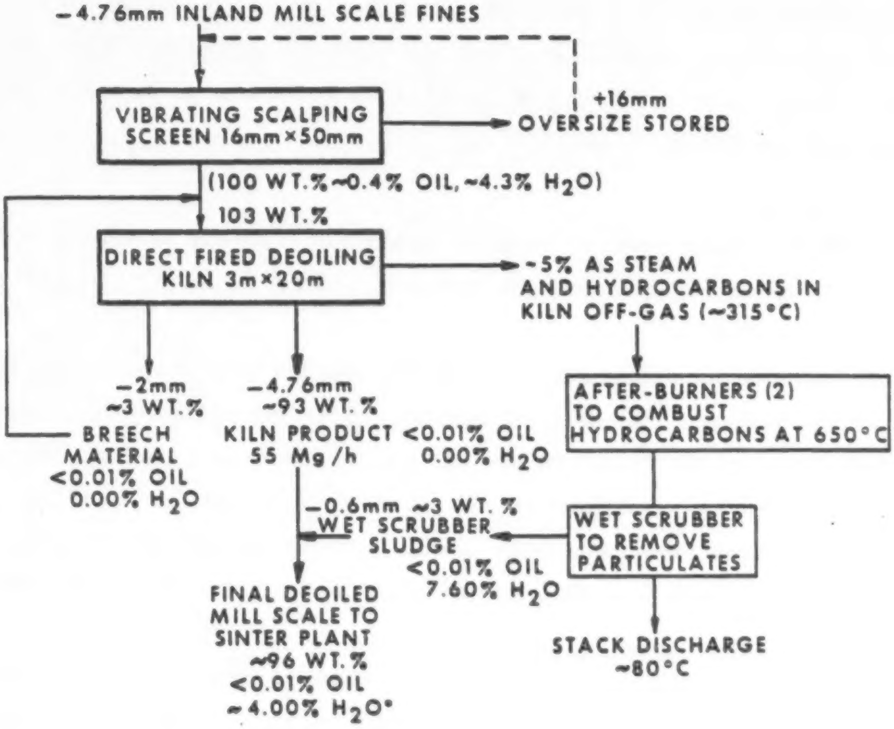
Mill scale is partly oxidized steel and, therefore, contains a high percentage of iron (72 to 75 percent), and no or low tramp element contamination. Without the oil content that accumulates, and looking only at the chemical composition, mill scale is a much better quality iron source than iron ore pellets.

Generally, mill scale is screened and the coarse fraction is used for direct recycle to blast furnaces. Mill scale fines (usually less than 4.76 mm (3/16 in.) were almost always in the past recycled to the sinter machines for agglomeration with other materials, followed by direct return to blast furnaces. In present practice, as indicated in one survey,(2) about 67 percent of the mill scale generated is recycled and about 33 percent or 1.7 million tonnes (about 1.9 million short tons) is landfilled annually in the U.S. because it is too oily for recycling. This oil mill scale, if charged to sintering operations, would result in air pollution and operational problems.

An Existing Reclamation Process For Oily Mill Scale--Thermal Deoiling

The only commercialized thermal method known for deoiling mill scale involves use of the direct-fired rotary kiln operated by the Luria Company for the Inland Steel Company. A schematic diagram of this process is shown in Figure 1.(4)

The rotary kiln deoiler is a counter-current reactor in which air is drawn from the mill scale exit end. The kiln is fired with natural gas and in passage through the kiln the mill scale is effectively deoiled



−4.76mm INLAND MILL SCALE FINES
VIBRATING SCALPING SCREEN 16mm×50mm
+16mm
OVERSIZE STORED
(100 WT.% ~0.4% OIL, ~4.3% H₂O)
103 WT.%
DIRECT FIRED DEOILING KILN 3m×20m
~5% AS STEAM AND HYDROCARBONS IN KILN OFF-GAS (~315°C)
AFTER-BURNERS (2) TO COMBUST HYDROCARBONS AT 650°C
−2mm
~3 WT.%
BREECH MATERIAL
<0.01% OIL
0.00% H₂O
−4.76mm
~93 WT.%
KILN PRODUCT
55 Mg/h
<0.01% OIL
0.00% H₂O
WET SCRUBBER TO REMOVE PARTICULATES
−0.6mm ~3 WT.%
WET SCRUBBER SLUDGE
<0.01% OIL
7.60% H₂O
FINAL DEOILED MILL SCALE TO SINTER PLANT
~96 WT.%
<0.01% OIL
~4.00% H₂O*
STACK DISCHARGE
~80°C

*MOISTURE ADDED FOR
DUST CONTROL DURING
HANDLING

Figure 1. Schematic of Commercial Direct-Fired Kiln Deoiling of Mill Scale Fines

from 0.4 to less than 0.01 percent residual oil. Two afterburners operating at 650 C (1200 F) and higher are used to assure complete combustion of any hydrocarbon vapors unburned in the kiln. The off gas from the afterburners is then scrubbed in a venturi scrubber to remove particulates. The wet scrubber sludge is added to the deoiled kiln product for return to the steel plant.

Energy Requirement--

The mill scale is received both wet and oily. The total energy usage as fuel is 0.22 G cal/tonne (810,000 Btu/short ton) of product. About 40 percent of the total fuel consumption is used in the afterburners for environmental protection.

Processing Costs--

No purchase cost or credits are taken for the incoming mill scale. No toll or royalty charges are considered because this information is proprietary.

For a production rate of 100,000 tonnes per year (sized for a typical steel plant), with new equipment, it is estimated that processing costs with steel plant labor rates are $35.93/tonne or product ($31.69/net ton). This is not an estimate of the processing costs for the Luria operation at Inland Steel which is about 5 times larger in capacity. The economics of scale are very pronounced in rotary kiln operations.

Environmental Appraisal Summary--

No stack data on emissions from this process were available for this study. However, the emissions can parallel those from other hydrocarbon-rich sources. If the afterburners on this process are closely controlled, it is expected that emission control will be acceptable and that no new environmental problems will be created.

An Emerging Reclamation Process for Oily Mill Scale--Solvent Washing

Colerapa Industries (Ravenna, Ohio) has a solvent washing pilot plant in operation for oily mill scale and mill scale sludge which employs the Duval-Pritchard process. Oily mill scale is "dry cleaned" at a rate of 1.8 tonnes/hour (2.0 ton/hour) using methylene chloride (CH_2Cl_2) as solvent. This solvent boils at 40 C (104 F) and has a density of 1.35 g/ml. The process flow sheet for this operation is shown in Figure 2. This process is claimed to handle mill scale of almost any particle size, oil level, or water content, with oil sludge containing

BLOCK DIAGRAM - MILL SCALE DEOILING PROCESS

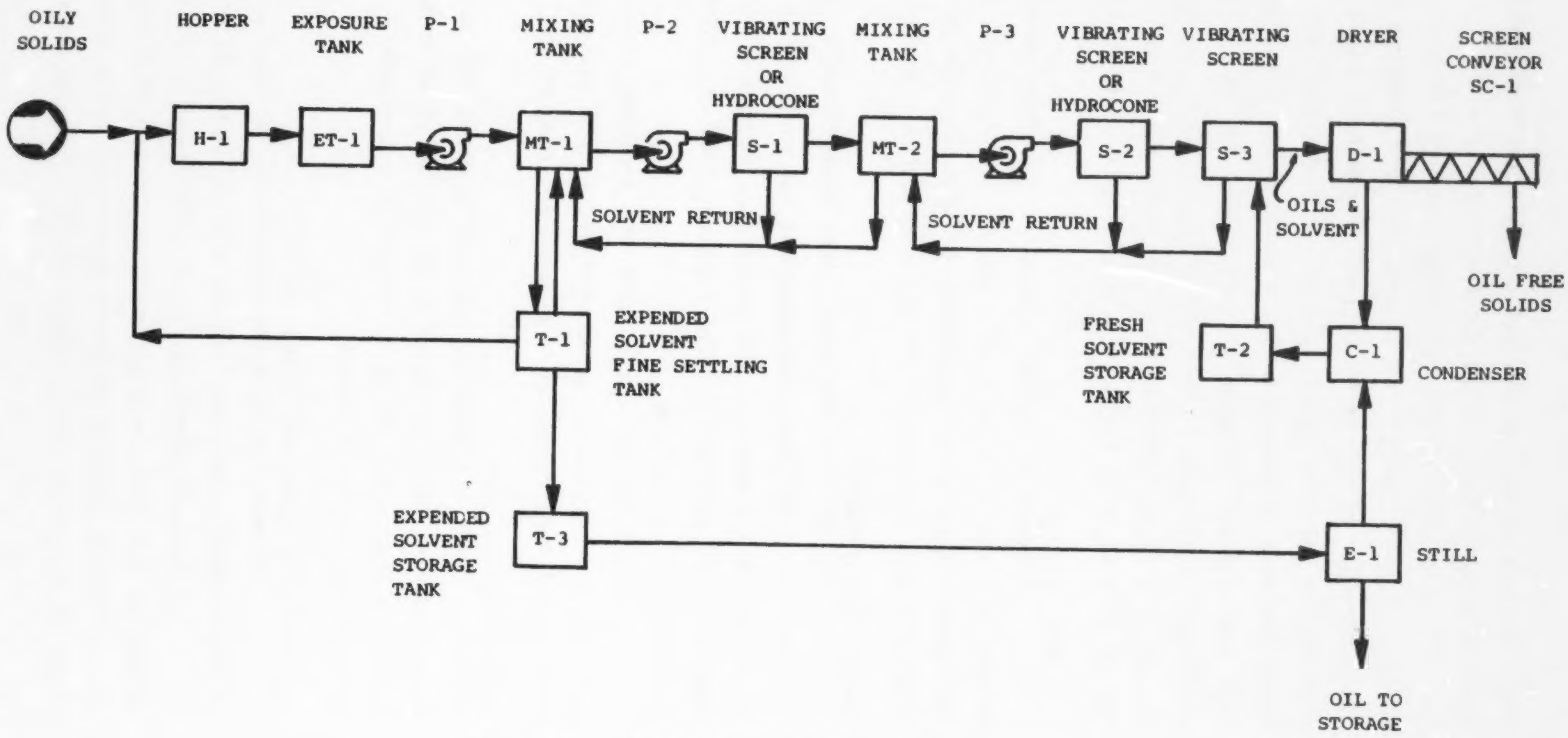


Figure 2. Block Diagram of Mill Scale Deoiling in Duval-Pritchard Process

small amounts of mill scale being particularly valuable because of the level of recoverable oil in the feed material.

The path of the mill scale through the process is counterflow to that of the solvent. As in ordinary dry cleaning of clothing, with discontinuance of agitation following treatment there is a density separation of the solvent, water, and oil at the end of the process. To collect final products (dry mill scale, solvent-free water, and solvent-free oil) each raw segregation segment is withdrawn and subjected to a heating operation to strip out the low-boiling solvent. Contaminated water is subjected to a stripping operation for solvent recovery, and solvent-contaminated oil is treated in a still to recover solvent and particle-free oils.

Material Balance--

Process literature indicates a solvent makeup of 0.6 pound of solvent per ton of product mill scale. If this loss can be maintained, the operation could be considered to have an emission rate less than that of a well-controlled dry cleaning establishment.

Energy Requirements--

The process developer takes energy credit for the oil recovered and the amount of water displaced and not evaporated. Reported energy purchased is 3.3 kwhr/ton for electrical energy and 0.07 G cal/tonne of feed (255,000 Btu/ton) for the fuel required for solvent evaporation and distillation.

With the assumption that the incoming scale can average 12 percent oil and 14 percent water, the net energy gain (mainly in recovered oil) is 1.7 G cal/tonne (6.2 million Btu/ton) of mill scale product.

Processing Costs--

Costs for removing oils and greases from mill scale by washing with a solvent were estimated to be $16.84/tonne or $15.28/ton. This assumes a credit for about 30 liters of oil (about 8 gallons) per ton of deoiled mill scale produced.

Environmental Appraisal Summary--

No emission data were available for this process so an evaluation of the potential gaseous, liquid, and solid wastes had to be made.

From the viewpoint of an environmental engineer, solvent vapor emissions from this process could be reduced to a very low level if special design considerations are given to solvent emission control in terms of equipment design (tightness) and equipment types. For example, efficient condensation of the low-boiling vapors may require refrigerated condensers. All exhaust pipes from the system may require activated-carbon filters. Favorable to the process is the fact that the listed toxic concentration for the selected solvent in air is higher than that for most commercial solvents that are routinely used. However, the solvent is a listed priority pollutant for water and any application of the process should include consideration of the environmental significance of residual methylene chloride in the water and losses to air and solids.

RECLAMATION PROCESS FOR STEELMAKING DUSTS

For U.S. steel production at the rate of 125 million tonnes/year (138 million tons), the amount of dust collected annually from the exhaust gases of the three types of steelmaking processes totals an estimated 2.2 million tonnes.(2) Of this quantity, only about 20 percent is recycled and about 1.8 million tonnes (2.0 million tons) is landfilled. This estimate includes landfilling of about 350,000 tonnes of electric-arc furnace steelmaking dusts and sludge that have been listed by the EPA as being hazardous.(3)

The majority of the steelmaking dust collected is not recycled because it contains contaminants that (a) are not removed during any agglomeration process, and (b) if recycled to blast furnaces (following agglomeration), would cause operating problems. With regard to blast furnace operations, the contaminants of concern are mostly zinc and alkalies. Of concern to the EPA are the lead, cadmium, and chromium contents in the steelmaking dusts. The source of these contaminants is the steel and iron scrap used in every steelmaking process, and the level of hazardous elements in steelmaking dust depends on the amount and type of scrap used in a particular steelmaking operation. Practically speaking, electric-arc steelmaking furnaces use 100 percent scrap charges and the steelmaking dusts collected at these furnaces can contain hazardous contaminants to levels of 4 percent lead and 0.05 percent cadmium. High chromium-content levels in steelmaking dusts are usually restricted to dust collected in alloy and stainless steel processing.

"Greenballing"--The Reclamation of Steelmaking Dust by Recycling to Steelmaking Furnaces

The literature in the 70's described a reclamation/recycle approach for contaminated steelmaking dusts which consisted of pelletizing the finely divided dust and recycling the pellets back to any steelmaking furnace. The term "greenballing" was used because the pellets had not been hardened but were "green" or freshly made.

In a steelmaking furnace charge, the iron oxides in green pellets are used as a substitute for iron-ore pellets and are utilized in slag formation and melt cooling. The zinc, lead, cadmium, and perhaps some alkalies in the scrap plus the reducible nonferrous oxides in the green pellets are reduced and some are vaporized, and collected in the standard dust collection equipment. Assuming complete collection of the volatile nonferrous oxides and no losses to the slag or molten steel, the nonferrous content in the steelmaking dusts should rise steadily during green pellet recycling. In theory, after a number of recycles, the nonferrous content in the steelmaking dust could be high enough to warrant periodic diversion of this dust to a nonferrous smelter. The continual buildup in zinc content in the collected dust during recycling has not occurred, indicating that there is a bleed from the system.

Discussions with personnel at various steel companies indicate that (a) the failure of the zinc content in the dust to steadily increase during recycling remains a mystery, and (b) all companies contacted have curtailed or discontinued reclamation via greenballing. Some companies indicate that greenballing has been curtailed because of the present low level of steel production and because of the increase in sulfur content in the steel upon recycling steelmaking dusts.

It is assumed that greenballing is being technically examined by steel companies for a more complete understanding and/or improvement. This process was therefore included in this study. The flow sheet of Bethlehem Steel's greenballing process is given in Figure 3.(5) As indicated in the foregoing text, the material balance on greenballing is being investigated. There is no information of the total energy requirement for this approach.

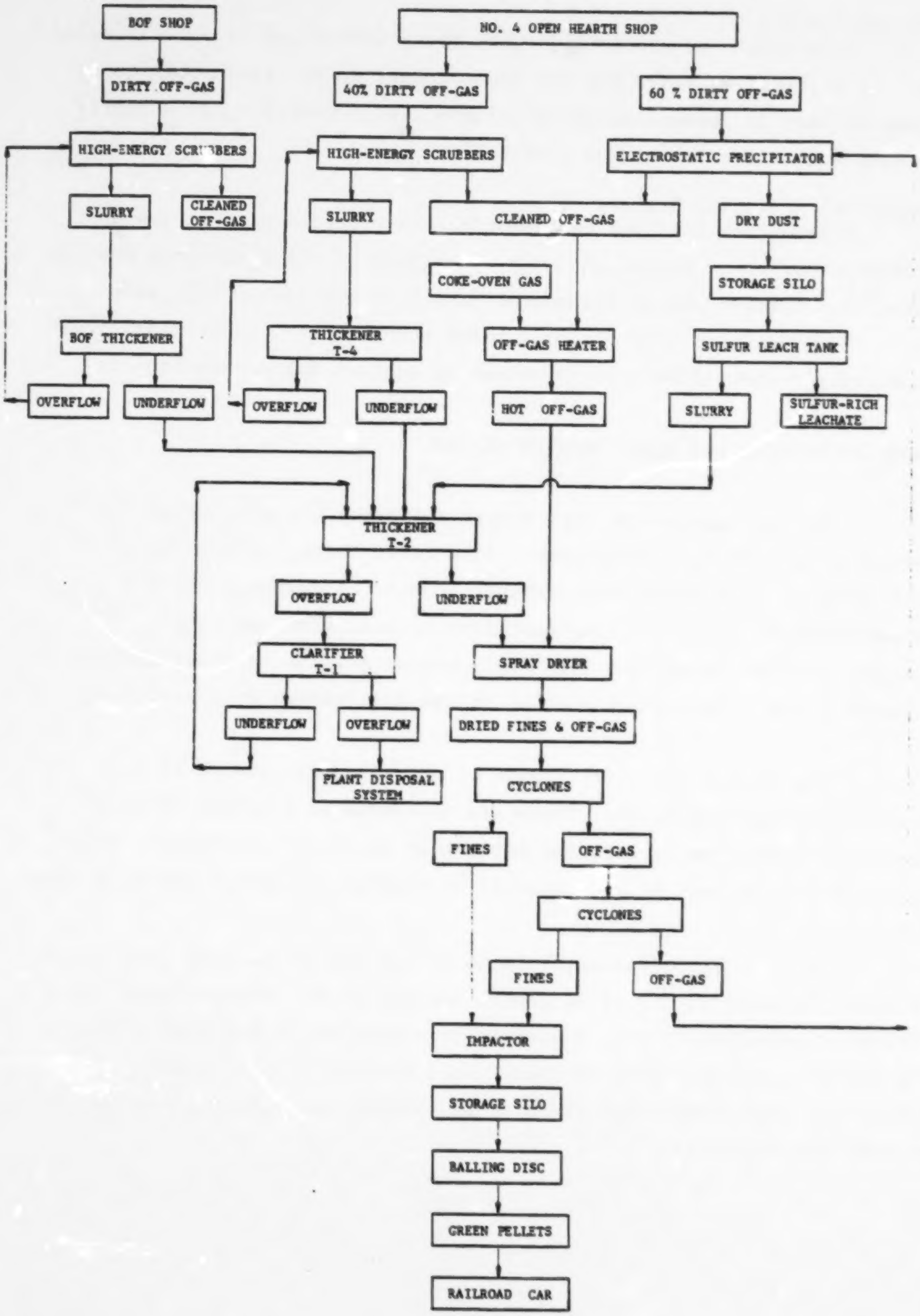


FIGURE 3. FLOW DIAGRAM OF BETHLEHEM STEEL CORPORATION'S GREENBALLING PROCESS FOR RECLAIMING STEEL-MAKING DUSTS. FIGURE WAS DRAWN BY BATTELLE.

Processing Costs--

An estimate of processing costs for greenballing is about $36.50/ tonne. If a credit is taken for the iron content in the green pellets as compared to that in commercial oxide pellets, the production costs nearly break even with the value of the greenballs.

Environmental Appraisal Summary--

Inasmuch as lead and cadmium normally vaporize with zinc when reduced with carbon or carbon monoxide, a balance of these elements must be obtained to determine the environmental impact of any losses or bleeds.

The fact that very finely divided compounds may be very difficult to completely recover from a large volume of exhaust gas causes concern.

RECLAMATION PROCESS FOR BLAST FURNACE SLUDGE

The top gas stream from almost all blast furnaces is passed through a series of dust collectors. In a first stage, mainly coarse dust is removed in a simple dust catcher (expansion chamber) and the dry dust consists mainly of fine particles of ore, flux, and coke. If the alkali content is not too high, this coarse dust is recycled through the sinter plant. The carbon content in the dust serves as a sintering fuel.

The second and third stages of gas cleaning consist of wet collection of fine particles. These are collected as a slurry which is subsequently dewatered to a sludge holding 20 to 25 percent water. Sixty to seventy-five percent of this dust is 44 microns or less in particle-size diameter.

In some blast furnaces, about 75 percent of the zinc that enters the blast furnaces in ore or in sinter reports to the blast furnace sludge. Continuous recycling of this sludge would result in an overload of zinc in a furnace, and operating problems would develop. Steel plants are landfilling this sludge when the zinc and alkali contents are considered too high for recycling.

About 22 percent of the blast furnace dust and sludge collected in the United States is not recycled to in-plant sintering operations. At least some of this dumping occurs because some steel plants do not have sintering operations.

Hydroclassification For DeZincing Blast Furnace Sludge

In Japan, the lead and zinc content of some blast furnaces sludge is higher than that reported in the United States. The lead content can reach a level of 0.7 percent and the zinc content can reach 7 percent.(6)

In 1974, Nippon Steel Corporation and Kowa Seiko Co. (a nonferrous processing company) began a joint study on utilizing nonferrous metal-bearing blast furnace sludge in processes "other than pyrometallurgical reduction".(6) The zinc and lead contents were found to be concentrated in the finer particle-size portion of the sludge. For example, about 80 to 90 percent of the lead and zinc compounds are concentrated in the portion of the sludge that is smaller than 44 microns in particle-size diameter. No plant data are available on the particle-size distribution of the alkali metals.

A wet classification system was then developed to separate out the nonferrous-bearing portion of the sludge to permit recycling of the "cleaned" portion. Laboratory and field tests indicated that the desired separation or beneficiation could be accomplished by means of hydroclones. The action of hydroclone equipment on a slurry is analogous to passing a gas and dust mixture through a dust-collection cyclone. In both instances, classification by centrifugal forces occurs.

By 1977, the wet-classification reclamation method for blast furnace sludge was in plant operation at the Kamaishi Works in Japan. The flow sheet of this process is shown in Figure 4.(6) At the Kamaishi Works, the slurry from the dust cleaning systems on 2 blast furnaces is adjusted

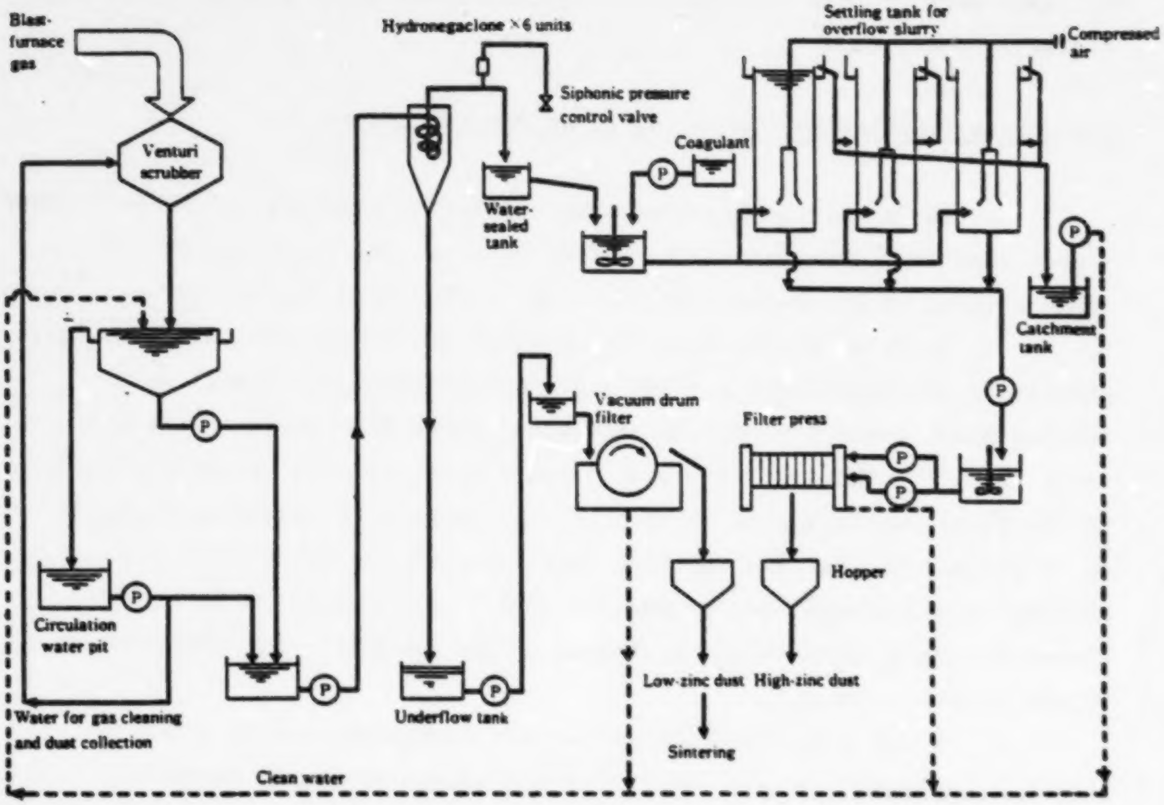


Figure 4. Flow Sheet of the Blast Furnace Sludge Processing Method at the Kamaishi Works in Japan

with water to have a 5 to 15 percent dust concentration. This slurry is passed through 6 parallel, upgraded versions of hydroclones. Each hydroclone has 75-mm (3-in.) inside diameter and the flow rate through the hydroclones is in the range of 20 to 100 l/minute (5 to 25 gal/minute).

The overflow slurry contains about 75 percent of the zinc in the feed material (and presumably most of the lead) and totals about 25 percent of the feed weight. The underflow contains about 83 percent of the original contained iron and 77 percent of the contained carbon. The underflow stream is filtered and is granulated into mini-pellets for use as a sinter strand raw material. The use of these high-carbon pellets reportedly resulted in a decrease of 2 kg (4.4 lb)/tonne in the use of coke breeze in the sintering operation.

The overflow material is allowed to settle and is then dewatered in a filter press. This nonferrous-bearing portion contains about 18 percent iron, 13 percent zinc, and 23 percent carbon. No information was obtained on the subsequent processing and the subsequent sale or disposal of this material.

Nippon Steel Company has indicated that while they are successful in reclaiming blast furnace sludge by wet beneficiation, they have not as yet been successful in using this approach to separate nonferrous compounds from steelmaking dusts.

Material Balance and Energy Requirement--

This classification operation is purported to be a very simple process with essentially 100 percent recovery of the original wet-collected blast furnace sludge. Relative to the other reclamation processes, the energy requirements for this process are considered negligible.

Processing Costs--

No attempt was made to estimate the low processing costs of this reclamation operation. The Japanese author labeled the development "an epoch-making resources utilization technique". From what is known of the process, it appears to be a "real winner". It can and is being used to recover iron and nonferrous values from landfilled blast furnace sludge storage. It would appear that this physical-separation reclamation process has the potential of being the starting point for eliminating the need to landfill about 750,000 tonnes of sludge annually in the United States.

Environmental Appraisal Summary--

It is anticipated that the bleed streams of waste water would have to be treated to remove the cyanide and water soluble organics. Such treatment technology is currently practiced by the industry.

It was judged that the emissions from this process appear controllable and there is no reason to believe that the process would introduce any new environmental problems.

PYROMETALLURGICAL, COREDUCTION RECLAMATION PROCESSES FOR RECLAIMING MILL SCALE, STEELMAKING DUSTS, AND BLAST FURNACE DUSTS

In Japan, there are seven or more rotary kilns in operation that reclaim steel industry, contaminated iron-bearing wastes. In this paper these processes are called coreduction operations because the contained iron oxides are reduced to value-added, direct-reduced iron (metallized iron) while some of the nonferrous oxide contaminants are also reduced. In this instance the reducible and volatile nonferrous elements are vaporized and are collected by means of the exhaust-gas dust collection system.

Within the various rotary kiln operations in Japan there are five different process variations of only minor importance to this study. Only the Kawasaki process is described and appraised here because it is the newest operation (1977) and presumably has the latest in dust collection equipment.

In the United States, the rotary kiln, coreduction approach for the reclamation of various iron-bearing wastes was examined and tested by Inland Steel and Heckett Engineering in the late 60's and early 70's.(7) To minimize future operating costs, the planning in this instance called for the use of a very large kiln for reclaiming wastes from four different steel plants in the Chicago area. No plant was ever built because the economics did not appear to be favorable and cooperation between competing steel companies was difficult to obtain. However, domestic interest in kiln reduction/reclamation continues.

Over the past decade, several process developers in the United States have been active in testing and promoting their approaches to cold bonding waste materials for recycling to blast furnaces. These approaches are substitutes for sinter agglomeration and differ from normal sintering or iron-ore pellet induration in that they use only a small amount of process heat. The most active cold-bonding technique developers are the PelleTech and Reclasource Corporations. PelleTech uses the Michigan Technological University (MTU) hydrothermal process. In this instance, the binding reactants are hydrated lime and silica that are activated for bond formation by autoclaving pellets for 1 to 2 hours at 2068 KPa (300 psig) steam pressure. Reclasource uses a pitch or asphalt binder addition and the agglomerates (briquets) are cured at about 260 C (550 F) to form a carbonaceous bond.

The early thrust of the PelleTech and Reclasource efforts was to (a) agglomerate mainly valuable mill scale, and (b) begin testing of their recycle agglomerates in blast furnaces to prove the strength of their agglomerates to potential buyers. This study, is concentrated on reclamation and not on recycling methods. However, by extension, the cold-bonding approaches show promise of agglomerating contaminated waste materials (such as steelmaking dusts) for input into some pyrometallurgical reclamation process. Reduction of cold-bonded agglomerates of contaminated waste materials in kilns, rotary hearths, or shaft furnaces would be akin to the coreduction practices developed by Inland Steel, Kawasaki Steel, and others, i.e., the products would also be direct-reduced iron (or smelted iron in a cupola operation) and by-product nonferrous oxide dusts.

The advantage claimed by both cold bonding organizations is that they are in a position to include (and retain) carbon inside of their agglomerates (during cold bonding). This will result in a much faster coreduction of the agglomerates upon heating. Faster, that is, than any coreduction using coke or char external to the pellets to produce the necessary carbon monoxide reducing gas. Technically speaking, the "high-speed" advantage claimed by the cold bonders has been well established. This technical advantage has yet to be translated into an economic advantage, but the odds appear favorable that it can be done. However, process speed only affects pyrometallurgical coreduction reclamation in the area of processing cost. All other appraisal factors for pyrometallurgical reclamation processes are about the same. Therefore, only the Kawasaki process and the environmental appraisal common to all coreduction processes are discussed here.

Kawasaki Rotary Kiln, Coreduction Reclamation

The newest "dust-reducing" plant installed by Kawasaki Steel (1977) is at the No. 2 plant in Chiba, Japan. The installation is rated at 1000 tonnes/day of material feed. This feed consists of pellets of combined blast furnace dust and sludge, oxygen steelmaking dust, and sinter dust. A generalized flowsheet for this plant is shown in Figure 5.

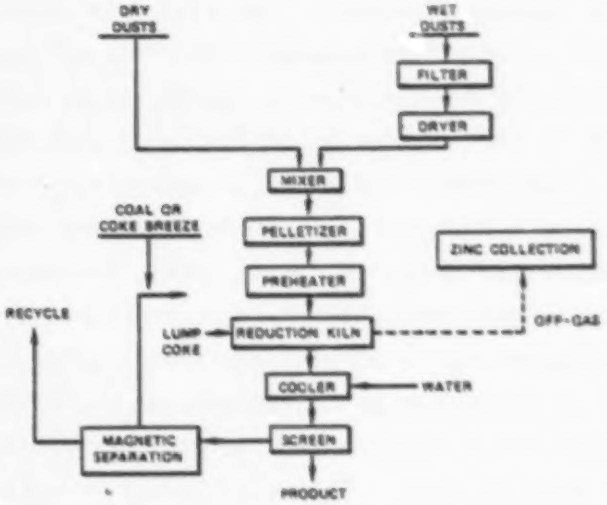


Figure 5. Generalized Flowsheet of Kawasaki Steel's Coreduction Process

Kawasaki Steel avoids the need for drying sludge by blending dry and wet materials (and by using supplementary, dry, fine iron ore when necessary). No information is available on the quantities and range in quantities of each waste material introduced into the process. Normally no binder is used. A grate preheater (downdraft) is positioned ahead of the kiln to dry and heat-harden the pellets of waste oxides. Pellet heating is done by means of the exhaust gases from the rotary kiln. Recent information indicates that the grate kiln heats the pellets to 1000 C (1,830 F) before they enter the kiln. The variation and level of the carbon content in the preheated pellets are not available.

The new Kawasaki kiln is 4 meters in diameter (16.5 feet) and 55 meters long (180 feet). The auxiliary heat is supplied with a heavy-oil burner positioned on the discharge end of the kiln. This burner is capable of firing 3,000 l/hour (793 U.S. gal/hr). Product recovery is about 600 tonnes/day. The feed to the kiln is a mixture of pellets and coke breeze. The coke breeze is used as a fuel and a source of reducing gas. The consumption rate of coke breeze is about 305 kg/tonne of product (610 lb/net ton of product). The operating temperature in the kiln is in the range of 1,100 to 1,200 C (2,000 to 2,192 F). No information was attainable on the gas velocity in the freeboard zone of the kiln interior. (See Environmental Appraisal.)

During passage through the kiln, the iron burden is metallized to the range of 90 to 95 percent. Also during coreduction, about 95 percent of the contained zinc is reduced (and blown out). Lead elimination is about 95 percent and elimination of alkalies is about 50 percent (also blown out). The metallized-iron product contains about 0.3 percent sulfur and 15 percent gangue, which minimizes the possibility of using the product in steelmaking.

The exhaust gases from the kiln pass through the grate preheater, through a water atomizing tower (to lower the gas temperature), and then through a huge electrostatic precipitator. It was not possible to obtain many details on the operation of this gas cleaning system.

According to one source,(8) the typical composition of the kiln exhaust dust of the Kawasaki coreduction kiln is as follows:

Element	Weight Percent
Zinc	14
Lead	4
Iron	26
Carbon	18
Sulfur	1
Sodium	1.7
Potassium	1.9

Kawasaki Steel states that this dust has little or no value to a buyer and is disposed of to the nonferrous industry. The above powder can be considered to be a low-grade zinc concentrate contaminated with iron. This problem of iron contamination of the nonferrous byproduct collected was also reported by Holowaty in 1971.(7)

Material Balance--

Kawasaki Steel Corporation has not published material balance data on their coreduction rotary kiln process. Of interest in a material balance would be the volume and composition of the off gases, as well as the dust loading in the off gas.

Energy Requirements--

The reported total fuel requirement per tonne of product is in the range of 3.5 to 4.2 G cal/tonne. This is equivalent to 12.6 to 15.1 million Btu/net ton of product or about 18.6 to 22.3 million Btu/net ton of metallic iron in the product. About one-third of the total fuel requirement is in the form of heavy fuel oil, and the remainder is coke breeze.

The zinc content of the pellets charged to the Kawasaki kiln is less than 1 percent and the fuel requirement for the reduction of the contained zinc and lead oxides is therefore negligible, i.e., the listed fuel requirement is almost entirely for the reduction of the iron oxides in the waste materials.

Process Costs--

To a major steel plant, the total reclamation costs using a coreduction process would be made up of the elements in the following equation:

SAVINGS	+	VALUE OF PRODUCTS	-	PROCESSING COST	=	TOTAL COST OR PROFIT
(Avoiding landfilling)		(Metallized iron + Nonferrous dust)				

Dealing with each element of cost in the preceeding equation, estimates were developed as shown in the following paragraphs.

Obtaining estimates for the cost of regulated landfilling proved to be a problem. Firm data on this topic may not as yet have been developed. Oral statements by steel company personnel place the 1980 landfill costs in the area of \$94 to \$100/tonne (\$85 to \$90/net ton), with multiplying increases expected in subsequent years. This cost level was somewhat confirmed by inquiries made to commercial landfill companies who are quoting a minimum price for regulated disposal at 4¢ per pound, delivered.

The maximum possible theoretical value of the iron content in metallized iron is equal to the selling price of the iron in high-quality, direct-reduced iron. Direct-reduced iron is listed for sale at \$130/tonne or \$116/net ton. Discounting for the lower iron content in the coreduced product brings the theoretical value (based on iron content only) to about \$97/tonne (\$88/net ton). However, metallized iron containing high gangue and sulfur is not suited for steelmaking operations and can only be recycled to blast furnaces. While it is a fact that high-quality direct-reduced iron charged to blast furnaces both decreases the specific amount of coke required per ton of product and increases the furnace production rate; the gangue in the coreduced product has heat requirements that act counter to these gains. As a judgment, the value of high-gangue, metallized pellets to a blast furnace is expected to be about \$70 to \$80/tonne or \$63.50 to \$72.50/net ton.

The by-product nonferrous oxides collected during any coreduction operation are not expected to have any value because of the high iron content (and related low zinc content) and objections to the presence of alkalies, chlorides, and other contaminants. Because disposal of this exhaust fume is also a problem, procedures (probably hydrometallurgical) will have to be developed to upgrade this material. Based on this expectation, no negative value was taken for the mixed nonferrous oxides.

Processing costs are estimated to be \$126/tonne or \$115/net ton. This is for a plant producing 100,000 annual tonnes of metallized product, starting with a total of 133,000 tonnes of waste materials. All unit costs are taken from published information, including the average employment cost of labor in the steel industry at \$19.11/manhour. Labor requirements are taken from Kawasaki information.

Total Costs or Profit

Repeating the basic equation:

SAVINGS	+	VALUE OF PRODUCTS	-	PROCESSING COSTS	=	TOTAL COST OR PROFIT

and filling in the derived numbers:

(1.33 x \$94)	+	\$80	-	\$127	=	\$78/tonne of product,profit \$70/ton of product, profit.

The element that causes the result to show a profit is the savings of \$125/tonne of product in not landfilling the wastes. Stated another way, if there were no substitute for the coreduction processes and the assumed savings in avoiding the cost of regulated landfilling are factual, the processing cost of a coreduction reclamation process could reach the level of \$205/tonne of product and theoretically "break even".

The data base for the above presentation of costs is weak and conditions did not permit any detailed cost analyses. However, the expected increased cost of landfilling will act as an incentive toward developing suitable reclamation processes.

Environmental Appraisal of Coreduction Operations

Information from Kawasaki Steel indicates that the flue gas released after the electrostatic precipitation contains between 0.001 and 0.03 g/Nm^3 of dust. Lead oxides, cadmium oxides (and presumably zinc oxide), and organic particulates (hydrocarbons) are below "identification limits".

As effective as the collection of particulates in the Kawasaki process appears to be, it may or may not be sufficiently effective to meet the U.S. primary ambient air quality standards for lead and particulate emissions of 1.5 $microgram/m^3$ and 75 $micrograms/m^3$ respectively--as measured at the plant property line.

The nonferrous metal emission from a coreduction process is likened more to that of secondary lead (or zinc) recovery processes in the United States. In these recovery processes the amount of stack gas being treated is about one-tenth the flow rate being treated in the Kawasaki process. This fact and the probable low concentrations of dusts in the effluent , as well as, the 200 C temperature of the gases entering the electrostatic precipitator, suggest a potential for poor collection efficiency of the nonferrous metal dusts (98 percent recovery claimed).

The fuel used in the Kawasaki process is heavy oil of unknown sulfur and ash content. Because of the high temperatures in the kiln and grate preheater, hydrocarbons in the exhaust gas from the fuel oil burner and volatile matter in the coke are expected to be consumed.

Insufficient information was available to make environmental assessments of coreduction operations. However, it was judged that these coreduction operations have the potential for unacceptably high nonferrous metal emissions. It is believed that this potential exists because of (a) the extreme fineness of the non-ferrous fume, and (b) the necessity to remove a small amount of fume from a very large volume of exhaust gases. The stack gases from coreduction operations should be measured to determine environmental acceptability for the United States.

The judgment on the environmental aspects of coreduction operations holds for all coreduction operations in which lead, cadmium, zinc, and alkalies are vaporized from the charge. Neither the method of waste agglomeration nor the method of heating the agglomerates has any bearing on this vaporization. The same vaporization would occur in rotary hearth furnaces and in shaft furnaces, including smelting of the agglomerates in cupolas.

PROCESS RANKING AND CONCLUSIONS

The reclamation processes considered and appraised in this study are ranked based on a criteria listing that includes:

- Waste-processing capability
- Consideration of possible environmental problems
- Overall reclamation economics
- Energy considerations

Following the outline of this paper, processes are classified by the type or types of waste that they can reclaim. The general ranking of these processes in qualitative terms is given in Table 2.

Conclusions

(1) Within the reclamation processes that can only reclaim oily mill scale, the emerging solvent-washing process may have apparent advantages in terms of:

  (a) Being able to process materials having a wider range of oil-to-scale ratios

  (b) Having a lower estimated processing cost primarily because it recovers oil instead of requiring oil or natural gas as fuel.

Because of the low boiling temperature of the solvent used in the solvent-washing process for mill scale, it may be necessary to include refrigerated condensers and traps to hold solvent emissions to an acceptable level. Given controlled operation of the afterburners in the rotary kiln, mill scale deoiling method; there is no concern about acceptable emission control or the development of any new environmental problems.

(2) Based on the limited information that is available on the Japanese physical classification process for blast furnace sludge, this process appears to have the attributes of a winning process in terms of:

TABLE 2. GENERAL RANKING OF RECLAMATION PROCESSES FOR OILY MILL SCALE, STEELMAKING DUSTS, BLAST FURNACE SLUDGE

Ranking Criteria Waste-Processing Capability	Mill Scale Only		Steelmaking Dusts Only	Blast Furnace Sludge Only	All Wastes (Mill Scale, Blast Furnace, and Steelmaking Dusts and Sludges
Process Type	Rotary Kiln (Pyro)	Solvent Washing	Greenballing (Pyro)	Physical Separation (Wet Classification)	Pyrometallurgical Coreduction
Status	Existing	Emerging	Once Existing Now in Abeyance	Existing in Japan	Existing in Japan. May be emerging in USA with cold bonding agglomeration.
Environmental Considerations(1)	[+]	[+]	[0]	[+]	[0]
Economic Considerations(2)	Moderate Cost	Low Cost	Moderate	Very Low Cost	High Cost, Profitable only by avoiding expensive landfilling
Energy Requirements	Moderate (Fuel Used)	Very Low (Oil Recovered)	Low	Neglible	High

(1) A [+] rating--From the information available about the process and the technology available to control related emissions, the process is judged favorable.

A [0] rating--Limited data on process and emission composition. It is judged that insufficient information is available to make environmental appraisals without further data.

(2) At a stated minimum cost of future landfilling of $100/tonne of waste, or more, all of the above processes are profitable on an overall basis when expensive landfilling is avoided. The qualitative judgment listed refers to processing costs.

(a) Eliminating the need for landfilling

(b) Being a true reclamation process in the recovery of iron and carbon units in one stream and concentrating (for further treatment) the nonferrous contaminants in the overflow stream

(c) Introducing no environmental problems

(d) Having a low processing cost and low energy requirement

(e) Being retrofittable to the dust and sludge processing systems of existing blast furnaces.

(3) Unfortunately, there is no known emerging process(es) geared to the simple reclamation of steelmaking dusts. The simple approach of recycling pelletized steelmaking dusts to steelmaking furnaces (greenballing) apparently requires further development because this method is not being practiced at this time.

Research and Development is definitely needed for reclamation methods that will suitably process only steelmaking dusts. Particular emphasis should be given to electric-arc furnace (EAF) steelmaking dusts--the one type of steelmaking dust that is listed as being hazardous. While EAF dusts are high in recoverable nonferrous resources, they unfortunately are low in iron content and very high in near valueless and relatively inert gangue content. With these characteristics, these dusts do not necessarily represent good feed material for any coreduction operation. The answer to the resource recovery from EAF dust is expected to be some new in-plant process that is economical on a small scale and is capable of recovering zinc compounds and removing or rendering harmless the hazardous nonferrous components. Favorable to any processing cost will be the savings in avoiding both landfilling and possible shipping costs. To the best of our knowledge no reclamation process for steelmaking dusts that is based on physical classification has been successful. However, further research efforts in this direction are suggested.

(4) There are existing and emerging processes that can process all of the iron-bearing wastes of interest to this study (mill scale, some steelmaking dusts, and blast furnace dust and sludges.)
All of these processes are pyrometallurgical coreduction operations. The existing processes use rotary kilns and the emerging processes are also considering shaft furnace smelting in cupolas and shaft furnace solid-state reduction (direct reduction). All of these pyrometallurgical processes reclaim contaminated wastes by vaporizing some of the contaminating nonferrous metals in wastes. Vaporization is followed by burning the volatilized elements and then stripping the finely divided fume (mainly oxides) from a large volume of exhaust gas. Until stack sampling data become available, it is necessary to be concerned about whether pyrometallurgical coreduction processes can meet the present standards for lead emissions and the future standards for cadmium emissions. Coreduction processes might eliminate the potential of a water pollution problem but could need further emission-control developments to avoid an air pollution problem.

(5) It would appear that for future reclamation processes for steel industry, iron-bearing wastes; methods other than pyrometallurgical reductions have greater appeal in terms of lower processing costs, fewer (if any) environmental problems, lower energy requirements, and possibly less sensitivity to the economics of scale. With the advent of low-cost, near-ambient temperature reclamation processes for mill scale and blast furnace sludge, a simple reclamation process for steelmaking dusts is becoming a definite need.

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HANDLING AND DEOILING OF ROLLING MILL SCALE AND SLUDGE--A PROFIT CENTER FROM A PROBLEM

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"Hazardous Waste" is a classification which has recently been expanded to include significantly more steel mill waste streams. Oil laden rolling mill scale and sludge is one type of waste which has been included in this now broader category. Management of these oily wastes has always been a difficult problem for the steel industry, but the EPA's new regulations make the problem even more complex.

Disposal costs have been soaring and will continue to do so as currently used sites are exhausted and more remote locations must be secured. Future water quality standards will probably result in a further increase in waste disposal costs.

The high iron content of oily wastes has long been recognized as valuable, but increasingly stringent air quality regulations have all but eliminated their reuse in sintering facilities. Agglomeration techniques have also been generally unsuccessful because of the oil content of these sludges. The many obstacles to their reuse, combined with the costs and complexities of disposal, create a complex problem for the steelmaker.

Colerapa Industries has developed a technique for dealing with waste sludges which affords the steelmaker a most attractive alternative to an otherwise bleak situation. The Colerapa system starts with oily waste handling at the point of initial collection, using proprietary equipment to hydraulically excavate and transport these sludges. A process system is then utilized which separates the iron units from the hydrocarbon contamination.

The complete process provides the steelmaker with five specific benefits:

1) Greatly improved solids collection efficiency.

2) Elimination of the problems normally associated with sludge excavation and transportation.

3) Significant, and in some instances, total, waste volume reduction.

4) Production of a high quality iron source, suitable for use in any agglomeration operation.

5) Recovery of oil from the reclaimed mill scale for reuse as fuel.

INTRODUCTION

The subject of this paper is the patented Duval-Pritchard handling and processing technology as it relates to the recovery of iron values produced during Rolling operations at Steel Mills.

The description given in this paper is of a Two Ton Per Hour Pilot Plant Facility used to develop the necessary design criteria for full scale operating plants to recover the iron values. These values vary in size and are mixed with oil and water. The material recovered is in the form of clean, dry iron oxide suitable for recycling back to an agglomeration operation and oil suitable for use as a fuel.

HANDLING AND DEOILING OF ROLLING MILL SCALE AND SLUDGE

All steel mills put steel slabs through a hot form rolling process. On a daily basis, valuable iron units are lost in every facility in the world.

THE PROBLEM

Throughout the hot strip rolling process, the slab, sheet, bloom, billet, or bar is being oxidized, cooled and washed with a high pressure water spray. When the hot steel is exposed to oxygen in the air, as well as the wash water, a layer of iron oxide is formed on the surface of the steel being rolled. This layer of oxides is called "mill scale" or simply, "scale".

As steel is rolled, this layer of scale is broken away and replaced by a new layer. Generation of this new scale occurs each and every time the size or shape of hot steel is changed.

As scale breaks away from the steel, it falls through the roll tables into a flume, or sewer, through which high velocity water is flowing. In addition to the scale and water, a large amount of lubrication greases and oils from the rolling machinery, along with other mill debris, find their way into the flume. The larger scale pieces become coated with oil while finer particles, water, grease and oil combine to form a sludge.

These combined materials pose a serious water pollution problem if they are discharged into a waterway. In order to control this pollution, settling pits and basins are used to collect these sludges and prepare the water for reuse or discharge. Much has been done during recent years in the design and construction of these collection facilities to increase collection efficiency. In addition, terminal treatment facilities have been constructed and installed in an effort to upgrade the quality of water at the discharge from collection pits.

These terminal facilities include lagoons, and filtration units. However, as with any collection facility, efficiency remains high only as long as the system is relieved of what it collects. Once collected, the sludge presents a double problem; how to relieve the collection facility, and what to do with the removed material.

EARLIER PRACTICE

Traditionally, scale drags, ejectors, and mobile cranes equipped with clamshell buckets have been used to remove materials from the collection facility. When these practices are used, the larger solids are removed and trucked to the mill for reuse in the iron-making operation. The smaller and more concentrated particles (which are more difficult to handle), found in the terminal lagoon and filter backwash, are disposed of by dumping in land fills.

The required installation of air pollution control systems at agglomerating facilities in the iron-making operation, has posed new problems involving the hydrocarbon or oil carryover. Thus, more of the total scale is unacceptable for reuse.

The basic concept used in the design of settling pits and basins is to create a quiescent body of water that slows the highly turbulent sewer flow, allowing the waterborne solids to settle, while permitting the lighter oil in the water to rise to the surface. Problems have arisen in the use of the traditional systems in that the quiescent conditions are disturbed during the excavation of the scale and sludge. The conventional approach to managing these sludges, then, is not a satisfactory solution to the problem.

HYDRAULIC EXCAVATION OF THE MILL SCALE

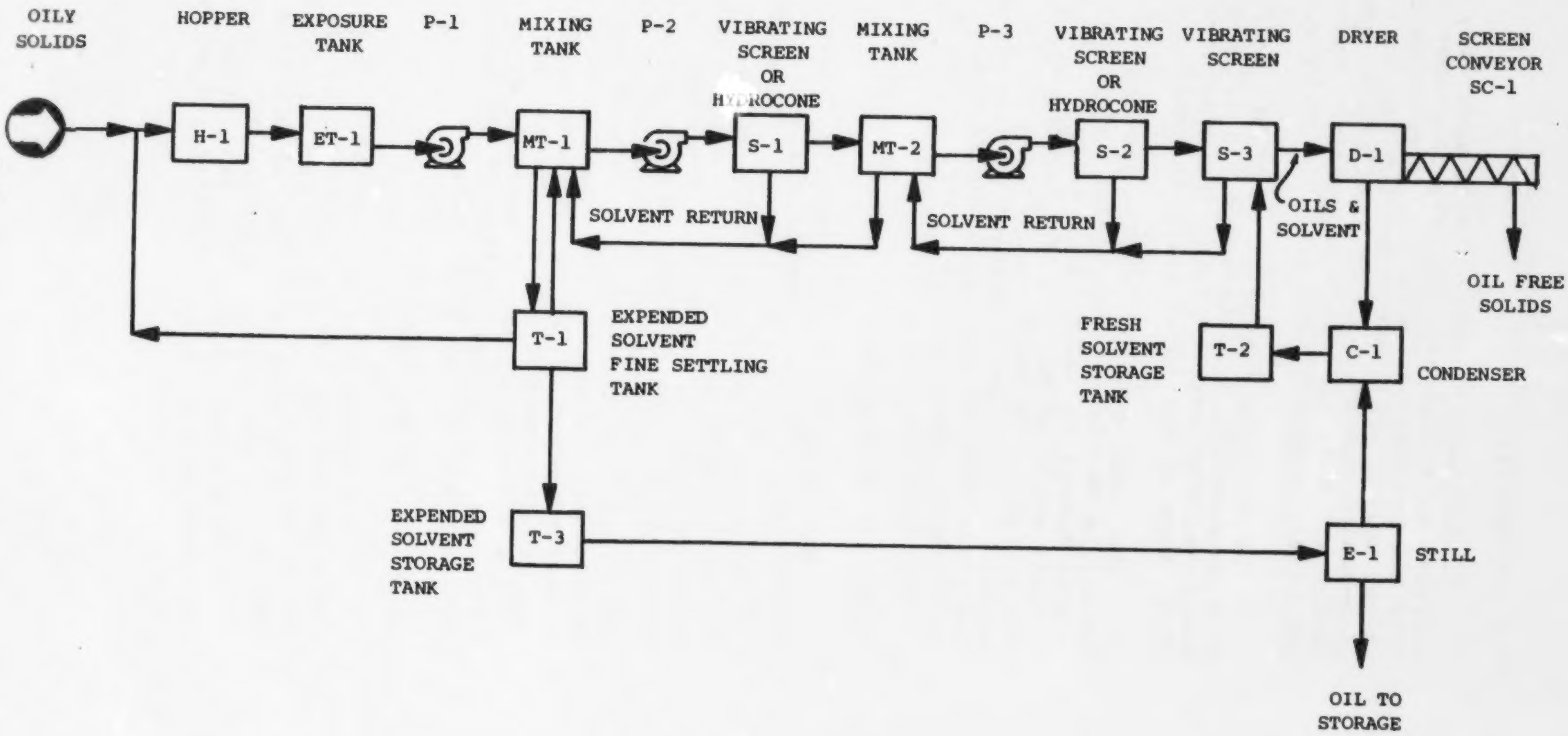
The development of Hydraulic Excavation Technology involved engineering equipment specifically designed for the variety of sizes and shapes of scale pits. The Hydraulic Excavator provides the quiescent conditions in the scale pit so necessary to promote the settling of solids as well as enabling oil to rise to the water surface for skimming. The lower turbulence resulting from hydraulic excavation increases the efficiency of the scale pit and reduces the load on the terminal water treatment facility. The result of this technology is reduced capital expenditure in scale pits and/or filters at the terminal treatment facility. The excavated material, which contains lower amounts of oil due to the reduced contact between the oil and the particles, is separated at the pit site by use of hydroclones and classifiers, while the water used in transportation of the solids is returned to the influent end of the scale pit.

DEOILING THE MILL SCALE

Development of this process of deoiling mill scale started years before the present emphasis on air emission and hazardous waste management began. It was evident that materials handled hydraulically were more free of oil than those handled with clamshells and drags. A water washing method was developed which extended the period that the mill scale was exposed to water. This resulted in the continued attrition of the oil from the particle and

FIGURE 1

BLOCK DIAGRAM - MILL SCALE DEOILING PROCESS



the production of a solid product with substantially lower oil content. Oils removed by this water wash process contain substantial amounts of water and very fine particles and have limited use without additional treatment.

Further improvements were made to the system through the use of detergents and alkaline solvent solutions; however, great care in reclamation of the water was required not only from the standpoint of the cost of these additives but also because of the carryover effects on the mill water.

The ultimate improvement was the development of the Duval-Pritchard process to convert hazardous hydrocarbon laden steel mill wastes to oil for use as a fuel or to be recycled, and to high grade iron concentrates for reuse in steelmaking.

The system is able to treat materials that are:

a) stockpiled

b) sludge-like and higher in oil and water contents

c) smaller sized

DESCRIPTION OF DUVAL-PRITCHARD SOLVENT EXTRACTION SYSTEM

This slide shows a process schematic of the pilot plant. The plant contains all planned recycle streams and will produce a totally deoiled mill scale product, plus a recovered oil product. Solvent recovery facilities are also included in the pilot plant design.

The mill scale is deoiled in two mixing stages of solvent washing, with a counter-current solvent flow. The two stages of solvent washing are followed by a solvent rinse to insure total deoiling. Spent solvent is evaporated and recovered for reuse in the process.

The mill scale is first fed into a hopper (H-1) with a front-end loader. The scale is transferred to an exposure tank via a screw conveyor: In the exposure tank the mill scale is slurried with spent solvent and pumped to the first stage mixing tank (MT-1). This mixing tank is an agitated vessel which provides total wetting of the mill scale with the solvent/oil solution. The mill scale slurry is then transferred from this first stage mixing tank to a second stage mixing tank through a transfer pump (P-2).

In order to achieve a good counter-current washing effect, the solids must be de-wetted between the first and second mixing stages. This is achieved in a hydroclone (S-1), in which the solids are de-wetted and sent to the second stage mixing tank. The liquids are then returned to the first stage mixing tank along with the overflow from the second stage mixing tank.

The second stage mixing tank (MT-2) is also agitated to provide complete wetting of the mill scale with a lean solvent solution. After mixing, the slurry is transferred to another hydroclone (S-2) which de-wets the solids. The solids then receive a final rinse on a vibrating screen (S-3). The liquids from S-2 flow back to the second stage mixing tank along with the rinse liquids from S-3.

The deoiled solids, with some entrained fresh solvent, are transferred from the rinse screen to a dryer (D-1) which has a steam jacket and steam heated screw. In this dryer, the solvent is vaporized and removed from the mill scale, leaving a dry, warm scale which is transferred to a product pile through a screw conveyor (SC-1). Vapors from the dryer are sent to a water-cooled condenser, where the solvent is re-liquefied. The liquid solvent then flows to the fresh solvent storage tank (T-2).

The oil rich solvent from the first stage mixing tank flows to the spent solvent fine settler tank (T-1). In this tank the fines settle to the bottom and the water contained in the mill scale floats to the top. The water is removed through a side-mounted drain and the fines are recycled to the process. The spent solvent is transferred to a spent solvent storage tank (T-3). The spent solvent storage tank adds surge capacity to the system and also gives one final stage for water separation from the solvent.

The spent solvent is recovered as follows: It is sent, on a batch basis, to an evaporator (D-1) which is steam jacketed; steam is supplied to the evaporator which boils off the solvent, leaving oil in the liquid phase; solvent vapors are condensed in the water cooled condenser (C-1) and sent to the fresh solvent storage tank. The oil is pumped to oil storage.

Each storage tank is sealed in order to minimize evaporation losses of the solvent. A package boiler system provides steam for the dryer and the evaporator.

The following is an example of the process energy balance based upon a typical analysis of materials recovered from the rolling mill waste water of steel mills. Iron oxides from 3/8" size to +400 mesh are typically found in such material.

The range of analysis for the three major components of the material is as follows:

	Content by weight in %
Oil and grease	.5% - 35%
Iron oxide particulates	45% - 98%
Water	4% - 30%

A weighted industry average analysis is as follows:

Oil and grease	12%
Iron oxide particulates	74%
Water	14%

If this material is to be used in a Sinter Plant briquetter or pelletizer for agglomeration, the ideal specifications would be:

Oil and grease	0%
Iron oxide particulates	100%
Water	0%

Note: The iron oxides in these wastes have a total Fe value of 72.4%, and an oxygen value of 27.6%

A typical analysis of iron ore concentrates as mined and processed by the principle iron ore producers in 62% Fe with 7% SiO_2, 28% O_2, and 3% other ingredients, including water.

The Duval-Pritchard process makes possible the recovery of the oil and grease, and the elimination of water from these hazardous wastes. The solids are, therefore, an ideal source of iron units.

The following is a calculation of the results of processing the industry average sample of material.

RAW FEED

Oil and grease	12% =	240#/Ton
Iron oxide particulates	74% =	1480#/Ton
Water	14% =	280#/Ton
TOTAL		2000#/Ton

ENERGY INPUTS

Electrical energy in BTU's =

3.3 KW/Ton X 3413 BTU/KW = 11,300 BTU/Ton

Heat Required

a) Distillation of expended liquid solvents = 105,000 BTU

b) Evaporation in dryer

Cycle = 45,000 BTU

Total Heat 150,000 BTU

TOTAL ENERGY INPUT 161,300 BTU/Ton

ENERGY CONSERVED

Oil recovered		
240# @ 18,500 BTU/#	=	4,440,000 BTU/Ton
Water displaced (not evaporated)		
280# @ 1,000 BTU/#	=	280,000
Total Energy Conserved		4,720,000 BTU/Ton

NET ENERGY PICK-UP

Total Direct Energy Conserved	4,720,000 BTU/Ton
Less Process Energy Required	- 161,300
Net Direct Energy Pick-up	4,558,700 BTU/Ton

Additional energy savings augment the benefits of this process are as follows:

1. SiO_2 content of ore concentrates must be eliminated in the Blast Furnace Slag, which requires heat. The process produces concentrates with no SiO_2 content.
2. Water content in the use of conventional ore results in a sensible heat loss. No water is contained in the finished product.
3. The elimination of other contaminants found in conventionally processed ore uses energy. This extra energy is not needed in the process, as there are no other contaminants present.
4. The use of the iron concentrate from the system reduces the amount of ore that must be mined.
5. The energy required to transport mined ore is lessened as that ore requirement is reduced.
6. Energy is also conserved in the reduced handling and managing of dumps to which these wastes are now being committed.

ECONOMICS OF THE PROCESS

Direct values derived from each ton of raw material (oily solids) fed to the process. Contents: 88% solids, 12% oil.

Market Values	Solids	$ 27/Ton
	Oil	$.50/gallon

Values from Solids			
	$27 x 88%	=	$23.76
Values from Oil			
	$\frac{.12 \times 2000\#/\text{Ton}}{6.5\#/\text{Gallon}} \times .50/\text{gal}$	=	18.46
Estimated Disposal Cost/Ton		=	4.50
	Total Values/Ton		$46.72
Less Estimated Process Costs/Ton			9.50
Net Direct Benefits of the Process			$37.22

The addition of the dollar savings of using the waste instead of disposing of it is a direct benefit of the process. Since the disposal costs vary with each location, the total benefits will be reflected by the difference in the actual disposal cost at the specific location.

CONCLUSION

This paper concerns a process for steel mill use to recover the oil and mill scale from environmentally hazardous material produced in rolling mill operations.

The system has no negative environmental impact.

The value of the process is directly proportional to the magnitude of the problem. A large quantity of oily waste can be converted from a costly hazard to a valuable material if the system is utilized. The use of hazardous waste to make valuable resources is a conversion of a negative to a positive factor in all rolling mill operations . . . . a problem to a profit.

SYMPOSIUM SUMMARY: Closing Remarks

Robert V. Hendriks
Symposium General Chairman
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

Closing Remarks

Robert V. Hendriks
Industrial Environmental Research Laboratory
Research Triangle Park, NC

During the past few days we have discussed a wide range of environmental topics relating to the iron and steel industry. We have heard discussions of advances in technology that have been made, of problems that are remaining, and of new problems emerging.

In his keynote address, EPA Assistant Administrator, Bill Drayton gave us a brief inside look at the way regulations are developed and described some of the Agency's efforts to develop regulations that will ensure adequate environmental protection at the lowest possible cost. Flexibility in regulations provides a positive incentive for developing better pollution control equipment and techniques.

The opening session also gave us some insight into an area given little attention during last year's symposium - innovative technology. Mr. Hollowaty of Inland Steel described the environmental aspects of a continuous coking process and Mr. Hirschhorn gave results of an Office of technology Assessment study describing potential new steelmaking technology (particularly, direct reduction), indicating important environmental considerations.

In the Air Session, we saw an emphasis on fugitive emissions, a relatively unknown area only a few years ago. Several years from now, we will likely have papers in areas where there is little work today, such as control of volatile organics and development of methods to improve the reliability of control equipment.

In the Water Session, emphasis was on the major water source - coke plants. We had papers on theory, design, and operation of biological treatment plants for cokemaking wastewaters. The most fruitful research area for the future appears to be in recycle and reuse of the large quantities of water used in the steelmaking process.

The Solid Waste Session was the briefest of all, although certainly no less important. As the air and water problems get solved and as RCRA is implemented, a greater emphasis will be put on disposing and using the materials removed from the waste streams.

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I am particularly gratified at the significant attendance at the symposium, despite the current poor economic climate, and the lively discussion that has taken place. This is a strong indication of the interest of all of us in improving environmental control in the steel industry. The significant progress within the last year in controlling pollution problems is also an indication of the rewards possible through cooperative discussions, planning, and research to improve environmental control in the steel industry. Only in this cooperative spirit will it be possible to develop the technology required to meet the industry's environmental control needs in a cost effective manner.

APPENDIX

Attendees

Ackermann	Kurt	J.	3426 East 89th Street, South Works	Chicago	IL	60617	U.S. Steel Corp.
Adams	Dick		101 Merritt 7, Air Correction Div.	Norwalk	CT	06856	UOP, Inc.
Alpago	Robert	T.	Bethlehem Plant	Bethlehem	PA	18016	Bethlehem Steel Corporation
Alton	Donald	E.	35 East Wacker Drive	Chicago	IL	60601	Kaiser Engineers, Inc.
Annamraju	Gopal	H.	11499 Chester Road	Cincinnati	OH	45246	PEDCo Environmental
Arent	David	V.	6th & Walnut Streets	Philadelphia	PA	19106	U.S. EPA, Region III
Armbrust	Robert	A.	600 Delaware Ave.	Buffalo	NY	14202	NY State Dept. of Envir. Conservation
Arnold	David		6th and Walnut Strerts	Philadelphia	PA	19106	U.S. EPA, Region III
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Basinski	Ralph	R.	900 Agnew Road	Pittsburgh	PA	15227	Jones & Laughlin Steel Corp.
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Bechard	Georges		1746 Massachusetts Avenue, N. W.	Washington	DC	20036	Canadian Embassy
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Bernhardt	Donald	J.	3839 W. Burnham Street	Milwaukee	WI	53215	Babcock & Wilcox Co.
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Brookman	Edward	T.	125 Silas Deane Highway	Wethersfield	CT	06109	TRC-Environmental Consultants, Inc.
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Clouse	Robert		Butler Works	Butler	PA	16001	Armco Inc.
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Crawford	David	A.	Allegheny County Airport	West Mifflin	PA	15122	Energy Technology Consultants, Inc.
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Gogola	Gordon		3 Blue Ball Road, P. O. Box 1100	Elkton	MD	21921	W. L. Gore & Associates
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Hendriks	Robert	V.	MD-62, IERL	Research Triangle Park	NC	27711	U.S. EPA
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Linsky	Benjamin		608 Arlington	Morgantown	WV	26505	A Different Air-Skyline
Littlewood	Roy		100 King St., W., Stelco Tower	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
LoBue	Joseph		10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
Lower	George	W.	Dept. of Metallurgical Engineering	Houghton	MI	49931	Michigan Technological University
Luton	John	W.	P. O. Box 96120, Industrial Road	Houston	TX	77013	Armco Inc.
Mahar	Kevin		Box A South Park Station	Buffalo	NY	14220	Donner-Hanna Coke Joint Venture
Malin	Morris	S.	P. O. Box 2063, Fulton Building	Harrisburg	PA	17120	Dept. of Environmental Resources
Mancke	Edgar	B.	P. O. Box 547	Portland	PA	18351	Edgar B. Mancke Associates, Inc.
Manda	John	G.	20th & State Streets	Granite City	IL	62040	Granite City Steel
Marteney	R.	E.		Fairless Hills	PA	19030	U.S. Steel Corp.
Maslany	Thomas	J.	6th and Walnut Streets, Curtis Bldg.	Philadelphia	PA	19106	U.S. EPA, Region III
Mazumdar	S.		10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
McCrillis	Robert	C.	IERL, MD-62	Research Triangle Park	NC	27711	U.S. EPA
Medwid	Grady	J.	913 Bowman Street (P. O. Box 247)	Mansfield	OH	44901	Empire-Detroit Steel Division
Melcer	Henryk		Box 5050, Wastewater Tech. Centre	Burlington, Ontario	CANADA	L7R 4A6	Environment Canada
Metzger	Daniel	J.	7777 Bonhomme Ave., Suite 1008	St. Louis	MO	63105	National Engineers and Associates
Micheletti	Wayne	C.	8501 Mo-Pac Blvd.	Austin	TX	78758	Radian Corporation
Middleton	Andrew	C.	440 College Park Dr.	Monroeville	PA	15146	Koppers Co., Inc.
Miller	A. Leslie		Koppers Building	Pittsburgh	PA	15219	Koppers Co., Inc.
Miller	Bruce		345 Courtland Street, N. E.	Atlanta	GA	30067	U.S. EPA, Region IV
Moore	Ben		345 Courtland Street, N. E.	Atlanta	GA	30067	U.S. EPA, Region IV
Moores	Charles	W.	One Broadway	Cambridge	MA	02142	Badger America, Inc.
Morganti	Ed		P. O. Box 460	Hamilton, Ontario	CANADA	L8N 3J5	DOFASCO
Moss	Mitch		442 River Road	Conshohocken	PA	19428	Keystone Coke Co.
Mount	David	R.	100 King Street, W.	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Mueller	Patrick	G.	1129 Bellwood Ave.	Bellwood	IL	60104	Faville-LeVally Corp.
Mura	William		4400 Fifth Avenue	Pittsburgh	PA	15213	Mellon Institute
Murphy	Samuel		U.S. 127 By-Pass South	Frankfort	KY	40601	Natural Resources & Env. Protection
Myers	Dennis	M.	100 S. Main, APCD	Pueblo	CO	81003	Colorado Dept. of Health
Neufeld	Ronald	D.	Dept. C. E., 939 BEH	Pittsburgh	PA	15261	University of Pittsburgh
Nicola	Arthur	G.	32nd Street	Pittsburgh	PA	15201	Pennsylvania Engineering Corporation
Nunno	Thomas		213 Burlington Road	Bedford	MA	01730	GCA Corporation
Oda	Terry		6th and Walnut Streets, Curtis Bldg.	Philadelphia	PA	19106	U.S. EPA, Region III
Olthof	Meint		3185 Babcock Boulevard	Pittsburgh	PA	15237	Duncan, Lagnese and Associates, Inc.
Osantowski	Richard	A.	5103 West Beloit Road	Milwaukee	WI	53214	Rexnord Corporation
Ottesen	John	A.	F. C. 416, S. Bedford Street	Burlington	MA	01803	Ion Physics Company
Parikh	Dilip		10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
Parker	Richard	D.	4901 Morena Boulevard, Suite 402	San Diego	CA	92117	Air Pollution Technology, Inc.
Patarlis	Thomas		4400 Fifth Avenue	Pittsburgh	PA	15213	Mellon Institute
Patton	James	D.	10 Chatham Road	Summit	NJ	07901	MikroPul Corporation

Penrose, Jr.	R.	G.	900 Agnew Road	Pittsburgh	PA	15230	Jones & Laughlin Steel Corp.
Peterson	Joseph	C.	515 S. Harmon Street	Indianapolis	IN	46225	Crown Environmental Control Sys., Inc
Pike	Daniel	E.	145 Cedar Lane	Englewood	NJ	07631	Neptune Air Pol, Inc.
Piper	Steve		213 Burlington Road	Bedford	MA	01730	GCA Corporation
Plaks	Norman		IERL, MD-62	Research Triangle Park	NC	27711	U.S. EPA
Plenderleith	James		P. O. Box 460	Hamilton, Ontario	CANADA	N1R 6V8	DOFASCO
Polglase	William	L.	MD-15	Research Triangle Park	NC	27711	U.S. EPA
Porter	Christopher	H.	Room 2112, ROB, 3001 Miller Road	Dearborn	MI	48121	Ford Motor Company, Steel Division
Pretti	H.	G.	65 East Elizabeth Avenue	Bethlehem	PA	18018	Wheelabrator-Frye, Inc.
Price	William	D.	3100 E. 45th Street	Cleveland	OH	44127	Republic Steel Corp.
Puchalski	Walter	J.	4636 Somerton Road	Trevose	PA	19047	Betz Laboratories, Inc.
Radigan	Patrick		20th & State Street	Granite City	IL	62040	Granite City Steel
Reggi	John		1911 Warwood Avenue	Wheeling	WV	26003	WV Air Pollution Control Commission
Rice	Michael		Homer Research Laboratory	Bethlehem	PA	18016	Bethlehem Steel Corporation
Ridolfi	James	P.	1875 New Hope Street	Norristown	PA	19401	PA Dept. of Environmental Resources
Riley	William	J.	Martin Tower	Bethlehem	PA	18017	Bethlehem Steel Corporation
Ruppersberger	John	S.	IERL, MD-62	Research Triangle Park	NC	27711	U.S. EPA
Saldanha	Geoff		100 King Street, West	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Schwartz	Stephen	M.	1000 16th Street, N.W.	Washington	DC	20036	American Iron & Steel Institute
Shackleton	Michael	A.	485 Clyde Ave., Energy & Env. Div.	Mountain View	CA	94042	Acurex Corporation
Shah	Raj		425 Volker Blvd.	Kansas City	MO	64110	Midwest Research Institute
Sharpe	Susan		IERL, MD-62	Research Triangle Park	NC	27711	U.S. EPA
Shaughnessy	Jack		10 Chatham Road	Summit	NJ	07901	MikroPul Corporation
Shibata	Hiroshi		345 Park Avenue	New York	NY	10154	Nippon Steel U.S.A., Inc.
Shiland	Thomas	W.	6th and Walnut Streets	Philadelphia	PA	19106	U.S. EPA, Region III
Shilton	David		P. O. Box 316	Pueblo	CO	81002	CF&I Steel Corp.
Shoup	Stefan	P.	3210 Watling Street, 2-110	East Chicago	IN	46323	Inland Steel Company
Simmons	Larry		P. O. Box 1899	Pittsburgh	PA	15230	Energy Impact Associates, Inc.
Sipe	James	P.	Chemicals and Pigments Building	Wilmington	DE	19898	E. I. DuPont Company
Sokolowski	Hank		6th and Walnut Streets	Philadelphia	PA	19106	U.S. EPA, Region III
Soo	S.	L.	144 Mechanical Engineering Bldg.	Urbana	IL	61801	Univ. of Illinois at Urbana-Champaign
Spawn	Peter	D.	213 Burlington Road, Technology Div.	Bedford	MA	01730	GCA Corporation
St. Pierre	George	R.	2041 N. College Road	Columbus	OH	43210	Ohio State University
Stagias	Nicholas	J.	154 Floral Avenue	Murray Hill	NJ	07974	Wilputte Corporation
Stebbins	Lloyd	H.	P. O. Box 8000, Four Echelon Plaza	Voorhees	NJ	08043	United Engineers & Constructors
Steiner	Bruce	A.	P. O. Box 600	Middletown	OH	45043	Armco Inc.
Steiner	Jim		485 Clyde Avenue	Mountain View	CA	94042	SEA, Division of Acurex Corp.
Sterner	Charles	J.	1465 Martin Tower	Bethlehem	PA	18016	Bethlehem Steel Corporation
Stewart	A.	D.	503 Queen Street East	Sault Ste. Marie, Ont.	CANADA	P6A 5P2	The Algoma Steel Corp., Ltd.
Stouch	James	C.	570 Beatty Road	Monroeville	PA	15146	GAI Consultants, Inc.
Sylvester	Mark		201 West Preston Street	Baltimore	MD	21231	Maryland Air Quality Program
Symons	Carl	R.	Homer Research Laboratories	Bethlehem	PA	18016	Bethlehem Steel Corporation
Szuhay	Lawrence	A.	P. O. Box 6778	Cleveland	OH	44101	Republic Steel Corp.
Telford	Anton	M.	2200 Churchill Road	Springfield	IL	62704	Illinois EPA
Thomas	Jean	G.	Somerton Road	Trevose	PA	19047	Betz Laboratories, Inc.
Tonelli	F.		Stelco Tower Phase 2	Hamilton, Ontario	CANADA	L8N 3T1	Stelco Inc.
Trembly	Martin	G.	25089 Center Ridge Road	Westlake	OH	44145	U.S. EPA, Region V
Tucker	A.	L.	3001 Dickey Road	East Chicago	IN	46312	Jones & Laughlin Steel Corp.
Tucker, Jr.	William	B.	P. O. Box 6778, Republic Bldg.	Cleveland	OH	44101	Republic Steel Corp.
Twork	John	V.	Homer Research Lab., Bldg. A/D326	Bethlehem	PA	18016	Bethlehem Steel Corporation
Uffner	Julia		550 Pinetown Road	Fort Washington	PA	19034	JACA Corp.
Vachon	Derek		867 Lakeshore Road, Box 5050	Burlington, Ontario	CANADA	L7R 4A6	Environment Canada
Vajda	Stephen		900 Agnew Road	Pittsburgh	PA	15227	Jones & Laughlin Steel Corp.

Vakharia	Nikil	K.	P. O. Box 6778	Cleveland	OH	44101	Republic Steel Corp.
Van Zuidam	Dick Michael		Emmastraat #1	Haarlem	HOLLAND		Ministry Nat'l Health & Pollution Cont.
Voruz	Ted		2901 Butterfield Road	Oak.Brook	IL	60521	Nalco Chemical Co.
Waechter	Ralph	W.	600 Kossman Building, 100 Forbes Ave.	Pittsburgh	PA	15222	PA Dept. of Environmental Resources
Wall, Jr.	William	T.	1901 S. Prairie Avenue	Waukesha	WI	53186	Envirex Inc.
Wallace	Anna	W.	P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Wang	Chingwen		Gen. Res. Inst. of Bldg. & Const.	Beijing	CHINA		Ministry of Metallurgical Industry
Watson	Ray		4901 Broadway	San Antonio	TX	78209	Railtex
Watson	Robert	G.	2901 Butterfield Road	Oak Brook	IL	60521	Nalco Chemical Co.
Waugh	John	H.	1930 Bishop Lane	Louisville	KY	40277	American Air Filter Co.
Wear	Myrl	R.	P. O. Box 600, 24 N. Main	Middletown	OH	45043	Armco Inc.
Weinberger	Jack		201 Schuylkill Avenue	Reading	PA	19601	Wagner Associates
Weinzapfel	Robert	B.	10 Chatham Ave.	Summit	NJ	07901	MikroPul Corporation
Westbrook	C. Wayne		P. O. Box 12194	Research Triangle Park	NC	27709	Research Triangle Institute
Whitehead	Martin	F.	628 W. Parklane Towers	Dearborn	MI	48185	Ford Motor Company
Wilhelmi	A.	R.	Military Road	Rothschild	WI	54474	Zimpro Inc.
Wilson	William		900 Agnew Road	Pittsburgh	PA	15227	Jones & Laughlin Steel Corp.
Wilson, Jr.	Leon	W.	125 Jamison Lane - MS 54	Monroeville	PA	15146	U.S. Steel Corp.
Winkler	Howard	A.	P. O. Box 6778	Cleveland	OH	44101	Republic Steel Corp.
Withrow	William		309 W. Washington, Suite 300	Chicago	IL	60606	Illinois Pollution Control Board
Wong-Chong	George	M.	700 Fifth Avenue	Pittsburgh	PA	15219	ERT Inc.
Xavier	James	F.	Environmental Control Department	Sparrow Point	MD	21219	Bethlehem Steel Corporation
Yan	Xingzhong		56 Block, Qing Shan, Hopei Prov.	Wuhan	CHINA		Ministry of Metallurgical Industry
Yocom	John	E.	125 Silas Deane Highway	Wethersfield	CT	06109	TRC-Environmental Consultants, Inc.
Yoel	W.		4625 Roanoke Boulevard	Kansas City	MO	64112	The Pritchard Corporation
Zachritz	W. Howard		7777 Bonhomme Ave., Suite 1008	St. Louis	MO	63105	National Engineers and Associates
Zwikl	James	R.	200 Neville Road	Pittsburgh	PA	15225	Shenango Incorporated